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The Se–H bond of benzeneselenols (ArSe-H): Relationship between bond dissociation enthalpy and spin density of radicals

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ABSTRACT

Bond dissociation enthalpies (BDE) of benzeneselenol (ArSe-H) and its *para* and *meta*-substituted derivatives are calculated using the (RO)B3LYP/6-311++G(2df,2p)//(U)B3LYP/6-311G(d,p) procedure. The computed BDE(Se–H) = 308 ± 8 kJ/mol for the parent PhSe-H is significantly smaller than the experimental value of 326.4 ± 16.7 kJ/mol [Kenttamaa and coworkers, J. Phys. Chem. 100 (1996) 6608] but larger than a previous value of 280.3 kJ/mol [Newcomb et al., J. Am. Chem. Soc. 113 (1991) 949]. The substituent effects on BDE's are analyzed in terms of a relationship between BDE(Se–H) and Mulliken atomic spin densities at the Se radical centers of ArSe (π radicals). Good correlations between Hammett's substituent constants with BDE(Se–H) are established. Proton affinity and ionization energy amount to PA(C_6H_5SeH) = 814 ± 4 kJ/mol and IE(C_6H_5SeH) = 8.0 ± 0.1 eV. IEs of the substituted benzeneselenols are also determined. Calculated results thus suggest that 4-amino-benzeneselenol derivatives emerge as efficient antioxidants.

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1. Introduction

Chalcogen-containing compounds play an important role in chemistry and biochemistry. The selenium element which is one of the chalcogens and belongs to the group 16 of the Periodic Table, occurs in four different valence oxidation states, namely Se^{6+}, Se^{4+}, Se^{2-} and Se^0. Selenium compounds are often used in the glass industry as decolorizing agents and in the rubber industry as vulcanizing agents. Selenium is also an essential trace element on humans and other species. Organoselenium compounds such as ebselen (1,2-phenyl-1,2-benzisoselenazol-3(2H)-one) [1,2], methyl selenol [3], dimethyl diselenide [4] and some selenium analogs [5–7] were found to exhibit significant antioxidant activities. Another basic selenium compound which has also attracted much interest is benzeneselenol C_6H_5SeH. The latter is the heavier congener of phenol (C_6H_5OH) and thiophenol (C_6H_5SH) and well known as one of the most efficient radical traps both in the gas phase and in solution, and plays a central role in radical reaction rate measurements [8–12]. The rate of radical trapping by benzeneselenol is characterized by the enthalpy change associated with the hydrogen atom transfer reaction. The formation and homolysis of the selenium–hydrogen bond in C_6H_5SeH are thus proved to be an important factor in many chemical and biochemical processes.

The homolytic Se–H bond energy of benzeneselenol, BDE(Se–H), was initially estimated to be 280.3 kJ/mol by Newcomb et al. [10]. Subsequently, this value was again determined experimentally by Kenttamaa and coworkers, who reported a value of BDE(Se–H) = 326.4 ± 16 kJ/mol (78 ± 4 kcal/mol) [12]. A discrepancy of about 46 kJ/mol (or 11 kcal/mol) between both experimental results for the BDE(Se–H) is in fact quite large, but it has not been reevaluated in the last 15 years. The lack of a reliable BDE(Se–H) value prompts us to reevaluate it using the current and appropriate quantum chemical methods.

The structure–antioxidant activity relationships of aromatic compounds YC_6H_4XH, where X = O, S, CH_2, SiH_2, NH,... have extensively been investigated and correlations between energies and structural parameters have clearly been established. The effects of the substituents Y on the activities are mainly exerted on the stability of the radicals generated [13–15]. Of the latter, the spin characteristics of the radical center emerge as an interesting parameter. As a matter of fact, homolytic bond dissociation corresponds to the breaking of a bond producing a radical species, and the spin density at the radical center has an important role in determining the stability of the resulting radical. The spin density in part describes the electronic structure of a radical and also the inherent delocalization of the unpaired electron and related conjugation effects. For the phenol derivatives (YC_6H_4OH), the changes of the BDE(O–H) with respect to various physical properties including the spin delocalization, were investigated by several

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groups [16–20]. Bond dissociation enthalpies and ionization energies of polyphenols have been the topics of many previous papers. The polyphenols are characterized by an extended conjugation and delocalization of the π-electrons involving the aromatic ring(s) and the substituents. They give rise to stable radical species upon the removal of a hydrogen atom or an electron. The odd electron appears to be delocalized over the entire molecule thanks to the planar geometry conformation. The stability of radicals is enhanced by the possibility to establish internal H-bonds between the radicalized oxygen atom and vicinal hydroxyl groups [21–24]. However, the behaviors of benzeneselenol and its derivatives as radical scavengers, antioxidants and related properties have not been studied yet. In this context, we set out to theoretically determine the trend of Se–H bond strengths in a series of ArSeH derivatives, along with the effects of various substituents at both the *para* and *meta* positions of the aromatic ring on the BDE(Se–H) values.

The purpose of the present study is twofold. First, we calculate the standard BDE(Se–H) values at 298.15 K of the parent C_6H_5SeH and two series of 3- and 4-substituted benzeneselenols YC_6H_4SeH with different Y substituents. In view of the discrepancy of experimental results on the BDE(Se–H) of C_6H_5SeH mentioned above, it is of importance to reevaluate it using reliable computations. Second, we attempt to find out if there is any relationship between the BDE(Se–H) with the spin densities at the Se centers of the ArSe radicals [19,25]. This could provide us with a better understanding of the origin of the substituent effect on Se–H bond dissociation energy in terms of spin delocalization. To establish such a relationship, we make use of the changes of the Mulliken atomic spin density (hereafter denoted as MASD) with respect to the changes of BDE(Se–H) when the substituents Y are placed at the *para-* and *meta*-position of the ring. In addition, the classical Hammett parameters are also employed to unravel the effects of the electron withdrawing and donating groups on the distribution of spin at the selenium center and thereby the stability of the radicals.

2. Computational methods

Previous studies abundantly showed that density functional theory (DFT) is one efficient and economic tool to determine with relatively high accuracy the BDEs and also the spin properties of free radicals [14,26–28]. One of the advantages of DFT is that the severe problem of spin contamination in the unrestricted Hartree–Fock (UHF) wavefunctions of the conjugated radicals can be avoided. DFT methods can thus be a suitable choice to remedy the usual spin contamination of the unrestricted MO formalism. Due to this reason, we use DFT methods to determine the BDE(Se–H) of benzeneselenols. All electronic structure calculations are performed using the Gaussian 03 (version D.01) suite of programs [29]. Geometry optimizations and harmonic vibrational frequency calculations are carried out using the 6-311G(d,p) basis set with several functionals. In order to obtain the correct electronic state of a radical species, a stability test is carried out for each radical structure. The enthalpy values are evaluated from the single point electronic energy calculations using larger basis sets at the 6-311G(d,p) optimized structures. We apply both unrestricted and restricted open-shell formalisms for the radicals at the corresponding basis sets. The Mulliken atomic spin densities (MASD) are taken from unrestricted open-shell UHF calculations at the selenium center and related atoms when necessary.

In order to determine some additional and relevant thermochemical parameters, the proton affinity (PA) of YC_6H_4SeH is calculated from the Eq. (1):

$$PA = H_f(Y - C_6H_4SeH) - H_f(Y - C_6H_4 - SeH_2^+) \quad (1)$$

The homolytic Se–H bond dissociation enthalpy value at 298.15 K for the molecule Y-C_6H_4-SeH is calculated from the Eq. (2):

$$BDE(Se-H) = H_f(Y - C_6H_4Se^\bullet) + H_f(H^\bullet) - H_f(Y - C_6H_4Se-H) \quad (2)$$

where H_f are the enthalpies of different species at 298.15 K. The energy of hydrogen atom is taken from the experimental value of −0.5 hartree. In all cases considered, the parent $C_6H_5Se\bullet$ radical is used as a reference for comparison.

The ionization energy (IE) of Y-C_6H_4SeH is defined as the smallest amount of energy required to remove an electron from a derivative. It is computed as the difference between the energies of its radical cation and the neutral molecule (Eq. (3)). For both neutral and radical cation species, zero-point energies (ZPE) determined from harmonic vibrational frequencies obtained at the B3LYP/6-311G(d,p) level are added, without scaling factor, to the electronic energy to obtain the energy E_0 at 0 K (Eq (3)).

$$IE(Y - C_6H_4SeH) = E_0(Y - C_6H_4 - SeH^{\bullet+}) - E_0(Y - C_6H_4SeH) \quad (3)$$

3. Results and discussion

3.1. Optimized geometry of C_6H_5SeH and its thermochemical parameters

The equilibrium geometry of the parent benzeneselenol is characterized by two lowest-energy conformations shown in Fig. 1a and Fig. 1b. Contrary to phenol and thiophenol, C_6H_5SeH is not planar. The hydrogen atom (at Se) in both optimized structures is located outside the benzene ring. Some selected bond lengths, bond angles and dihedral angles of both conformers obtained using different functionals are given in the Supplementary information (SI) file.

The C–C bond distances within the aromatic ring and the C1–Se bond length obtained by four DFT functionals are quite similar to each other. The length variation is about from 0.001 to 0.005 Å when using B3LYP, B3PW91, PBE1PBE and BMK functionals. A significant difference occurs only on the bond distance of C1–Se and the dihedral angle of C2C1SeH. The bond Se–H in the first conformation (Fig. 1a) is almost perpendicular to the ring whereas it is closer to the plane in the second conformer (Fig. 1b). Thus, rotation of the Se–H bond around the C1–Se axis corresponding to the two ground states are found at the dihedral angle (C2C1SeH) of about 77 and 38 degrees, as optimized at the B3LYP/6-311G(d,p) level of theory. The two conformers have almost the same energy content with an energy difference of only 0.2 kJ/mol in favor of the first one. The planar form is a transition structure for rotation connecting both conformers with a tiny energy barrier of about 1.0 kJ/mol.

Referring to the first conformer (Fig. 1a), we calculate a basic thermochemical property of benzeneselenol, namely its proton affinities. The proton affinities at the four different positions are calculated using the B3LYP, B3PW91, PBE1PBE and BMK functionals in conjunction with the 6-311G(d,p) and 6-311++G(2df,2p) basis sets. The results listed in Table 1 point out that the preferential site of protonation in benzeneselenol is predicted at the *para* carbon of the ring. The B3LYP, B3PW91 and PBE1PBE calculated PA at this site are rather close to each other, being 815, 818 and 812 kJ/mol, respectively. However, the BMK functional generates the PA value at the *para*-C position much lower than three above DFT functionals by 7–14 kJ/mol. It is well known that the hybrid B3LYP functional provides reliable PAs for benzene derivatives. Based on the calculated B3LYP values in Table 1 with the two basis sets, we propose a PA of benzeneselenol in the range of 814–818 kJ/mol.
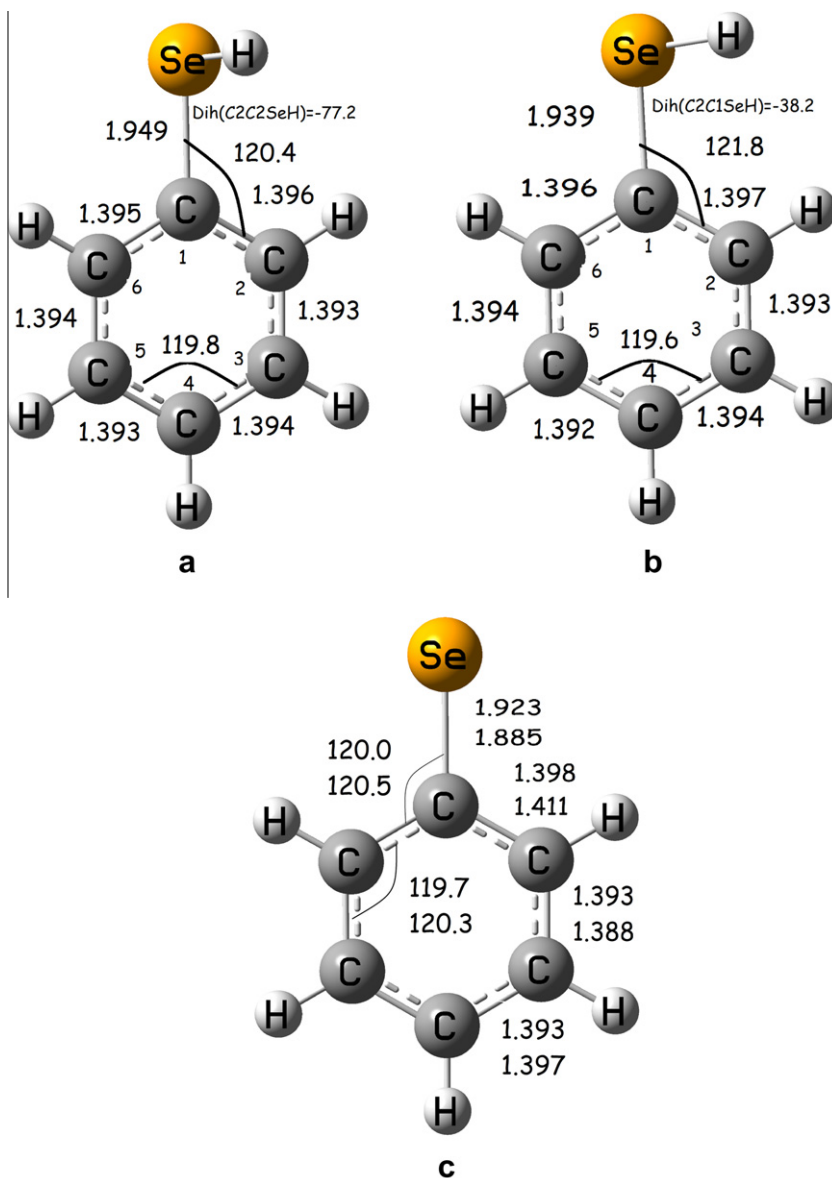
Fig. 1. Optimized geometries of two conformations of benzeneselenol (B3LYP/6-311G(d,p)) and of the $^2A'$ (upper values) and $^2A''$ (lower values) radical using (U)B3LYP/6-311G(d,p) calculations.

Table 1
Proton affinities of benzeneselenol at different sites using DFT functionals, values in kJ/mol.

Protonation site	B3LYP		B3PW91		PBE1PBE		BMK	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Se	794.8	794.4	798.9	799.5	793.9	794.0	784.9	787.9
C2 ortho	803.4	799.9	804.6	803.2	798.3	796.3	791.0	791.1
C3 meta	761.5	758.9	762.0	761.7	755.6	754.7	742.9	742.0
C4 para	817.1	814.7	818.7	818.2	812.6	811.7	804.8	806.1

(1) Using 6-311G(d,p) basis set; (2) using 6-311++G(2df,2p) basis set.

3.2. Bond dissociation enthalpy of benzeneselenol

The benzeneselenol radical exhibits, within C_s symmetry point group, two different lower-lying electronic states, namely $^2A'$ and $^2A''$. Selected optimized geometrical parameters given in Fig. 1c of the benzeneselenol radical point toward significant differences between them, especially in the C1–Se bond length. Other differences include as expected the MASDs at the selenium radical center. For the $^2A'$ state, the C1–Se bond length and MASD amount to 1.923 Å and 1.0 electron, whereas the $^2A''$ state has an optimized C1–Se distance of 1.885 Å and the MASD of 0.8 electron (UB3LYP/6-311G(d,p)). Accordingly, while in the σ-state $^2A'$, the unpaired electron is fully localized on selenium atom, in the π-state $^2A''$ it is in part delocalized into the ring.

It turns out that the $^2A''$ π-state is the lowest-lying electronic state of the C_6H_5Se radical. It is about 30 kJ/mol more stable than

Table 2
Calculated BDE(Se-H) of C_6H_5SeH using different methods (kJ/mol)[a].

DFT functional	BDE(Se-H) of C_6H_5SeH		
	6-311G(d,p)	6-311G++(2df,2p)	
	(U)	(U)	(RO)
B3LYP	301.4	303.8	307.6
B3PW91	291.2	292.9	297.2
PBE1PBE	278.9	280.8	286.1
BMK	289.7	291.6	296.7

[a] These values are calculated using the H's energy of −0,5 hartree. The BDE(Se–H) value is computed referring to the lowest-lying state $^2A''$ of Ar–Se radical. The experimental value of 326.4 ± 16.7 kJ/mol from Ref. 12.

the σ-state $^2A'$ counterpart. Although both states are rather closely lying, they could generate two distinct BDE(Se–H) values for benzeneselenol. The first BDE which corresponds to the lowest-lying state $^2A''$ is calculated at 307.6 kJ/mol (value at (RO)B3LYP/6-311++G(2df,2p)). The second BDE(Se–H) value, related to the $^2A'$ state, amounts to 332.0 kJ/mol at the same level and is apparently closer to the experimental value of 326.4 kJ/mol [12].
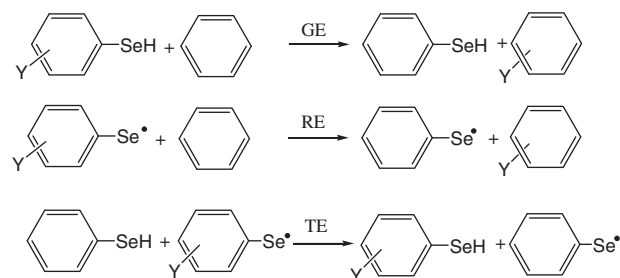
In previous studies, the restricted formalism (RO)B3LYP/6-311++G(2df,2p) procedure has been shown to predict accurately the BDE(X–H)'s of many aromatic systems [30–33]. However to ensure the reliability of this method for the compounds containing selenium atom, we first use the DFT functionals mentioned above along with the 6-311G(d,p) and 6-311++G(2df,2p) basis sets to calculate the BDE(Se–H) of C_6H_5SeH. The computed BDE(Se–H) results referred to the lowest-lying $^2A''$ state are listed in Table 2. These results clearly indicate that BDE(Se–H) values generated by a series of DFT functionals including the B3LYP, B3PW91, PBE1PBE and BMK are considerably smaller as compared to the most recent experimental one. Four calculated values for BDE(Se–H) in Table 2 are however consistent with each other. On the basis of the lowest-lying $^2A''$ electronic state of benzeneselenol radical, we strongly recommend the value BDE(Se–H) = 308 ± 8 kJ/mol for C_6H_5SeH computed using the reliable (RO)B3LYP/6-311++G(2df,2p) method. This value is smaller by about 18 kJ/mol than the experimental estimate of 326.4 ± 16.7 kJ/mol reported by Kenttamaa et al. [12]. However, our calculated BDE(Se–H) value is also larger than the earlier experimental value of 280.3 kJ/mol (or 67 kcal/mol) estimated by Newcomb and coworkers [10]. As mentioned above, a possible explanation for the discrepancy is that in the experiment carried out by Kenttamaa et al., the higher-lying electronic $^2A'$ state was probably generated and characterized, whereas the ground $^2A''$ state was produced in the experiment by Newcomb and coworkers. Nevertheless, we could not usefully comment on the details of these earlier experiments.

Scheme 1.

3.3. BDE(Se–H) of benzeneselenols with substituents at the para and meta ring positions

One of the parameters characterizing the activities of a good antioxidant is the hydrogen transfer mechanism. This redox reaction corresponds to a homolytic dissociation of an X–H bond, which is in this case of the Se–H bond. Since the substituents on the ring basically affect its molecular properties, it is crucial to understand how the BDE(Se–H) values change with the substituents at the para and meta-carbon positions of benzeneselenol ring, as well as in comparison to the related BDE(X–H) values of phenols and thiophenols.

Table 3 summarizes the calculated BDE(Se–H) results for both series of para- and meta-substituted benzeneselenols using the RO-B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) model. The changes in BDE(Se–H) values, as defined by ΔBDE(Se–H) = (BDE(YC_6H_4SeH) – BDE(C_6H_5SeH), for different substituents in going from the parent benzeneselenol to a substituted benzeneselenol are also given in Table 3. For para-substituted benzeneselenols, electron donating (ED) groups such as CH_3, OCH_3, NH_2, $N(CH_3)_2$ at the para position tend to sharply reduce the BDE(Se–H) value. Considerable deviations of −17.7 kJ/mol and −14.7 kJ/mol are seen for $N(CH_3)_2$ and NH_2 substituents, respectively. Electron withdrawing (EW) groups such as CN, CF_3, and NO_2 actually increase the BDE(Se–H) values by 7–12 kJ/mol. For meta-substituted benzeneselenols, the effect of the ED group is less clear-cut. The calculated BDE(Se–H) values for $4CH_3$-C_6H_4SeH and $4NH_2$-C_6H_4Se-H are seemingly unchanged with respect to the parent benzeneselenol. The EW groups still increase the BDE(Se–H) by less than 5 kJ/mol. The effects of F and Cl-substitutents at the para and meta ring positions occur in opposite directions. At the para position they slightly reduce the BDE(Se–H) from the parent benzeneselenol, but at the meta position, they increase it by about 4 kJ/mol. The effects of substituents on the BDE(Se–H)s follow a pattern similar to those of BDE(S–H)s of thiophenols as well as those of BDE(O–H)s of phenols [30].

Table 3
Calculated BDE(Se–H) values for para- and meta-substituted benzeneselenols using the ROB3LYP/6-311++G(2df,2p) method, kJ/mol.

Substituents	4Y-C_6H_4Se-H, kJ/mol		3Y-C_6H_4Se-H, kJ/mol		ΔBDEp-m[b]
	BDE(Se-H)	ΔBDE(Se-H)[a]	BDE(Se-H)	ΔBDE(Se-H)[a]	
H	307.6	0.0	307.6	0.0	0.0
F	305.4	−2.2	311.7	+4.1	−6.3
Cl	306.5	−1.1	311.4	+3.8	−4.9
CH_3	304.4	−3.2	307.6	0.0	−3.2
OCH_3	298.8	−8.8	310.4	+2.8	−11.6
NH_2	292.9	−14.7	307.6	0.0	−14.7
$N(CH_3)_2$	289.9	−17.7	307.0	−0.6	−17.1
CN	315.6	+8.0	313.8	+6.2	1.8
CF_3	315.1	+7.5	312.5	+4.9	2.6
NO_2	319.5	+11.9	314.5	+6.9	5.0

[a] ΔBDE = BDE(Y-C_6H_4Se-H) – BDE(C6H5Se-H).
[b] ΔBDEp-m = BDE(4Y-C_6H_4Se-H) – BDE(3Y-C_6H_4Se-H).

Table 4
Calculated radical effect (RE), ground state effect (GE) and total effect (TE) of *para*- and *meta*-substituents at (RO)B3LYP/6-311++G(2df,2p) (kJ/mol).

Y	4Y-C$_6$H$_4$SeH			3Y-C$_6$H$_4$SeH		
	RE	GE	TE	RE	GE	TE
H	0	0	0	0	0	0
F	0.6	−1.6	2.2	−3.8	0.3	−4.1
Cl	−0.4	−1.5	1.1	−4.0	−0.2	−3.8
CH$_3$	3.9	0.7	3.2	1.4	1.4	0.0
OCH$_3$	9.8	1.0	8.8	−1.3	1.5	−2.8
NH$_2$	17.3	2.6	14.7	2.1	2.1	0.0
N(CH$_3$)$_2$	21.6	3.9	17.7	3.5	2.9	0.6
CN	−6.3	1.7	−8.0	−8.0	−1.8	−6.2
CF$_3$	−6.3	1.3	−7.6	−5.9	−1.0	−4.9
NO$_2$	−9.0	2.9	−11.9	−9.2	−2.2	−7.0

A negative sign (−) indicates a destablization whereas a positive sign (+) indicates a stabilization. Accordingly, the TE's are equal to the ΔBDE(Se–H)'s given in Table 4 but having opposite sign.

Table 3 clearly indicates that the effect of a substituent also changes with its position on the ring. The largest difference between BDE(Se–H) at *para* and *meta* positions is found for the strong ED groups such as CH$_3$, OCH$_3$, NH$_2$, N(CH$_3$)$_2$ and then for the F- and Cl-atoms. On the basis of this point, a strong electron donating group should be attached at the *para* position rather than at the *meta* one of the ring when designing a strong antioxidant.

To understand further the effect of a substituent on the strength of the Se–H bond, we calculate the ground state effect (GE), radical effect (RE) and total effect (TE = RE − GE) from the reaction enthalpies of the exchange reactions shown in Scheme 1.

The GE effectively tells us how the ground state stability of benzeneselenol changes with respect to substituents at *para* and *meta* postions, whereas the RE indicates the same effect on the stability of the resulting radical. The calculated GE/RE/TE values are given in Table 4.

Results of Table 4 can explicitly be illustrated by a diagram shown in Scheme 2. It can be observed that the F and Cl atoms at the *para* substitutions induce an insignificant effect on the stability of the parent 4Y-C$_6$H$_4$SeH as well as the corresponding radicals. Both effects are estimated to be within 1–2 kJ/mol with the opposite signs. As a result, the total energy becomes slightly positive. In the case of ED groups, the total effects are dominated by the radical stability rather than the parent one. Although ED groups tend to stabilize both the parent and radical species, the RE values are found to be larger than the GE counterparts. Therefore, the resulting TE values remain considerably positive. In the meantime, the EW groups stabilize the parents but not the radicals. In this case, the GE possesses a positive sign and the RE has a negative sign. However, the latter parameter is larger thus leading to a negative TE value.

For the *meta* substitutions (Scheme 2b), both F and Cl atoms induce a small effect on GE values. They also destabilize the radicals,
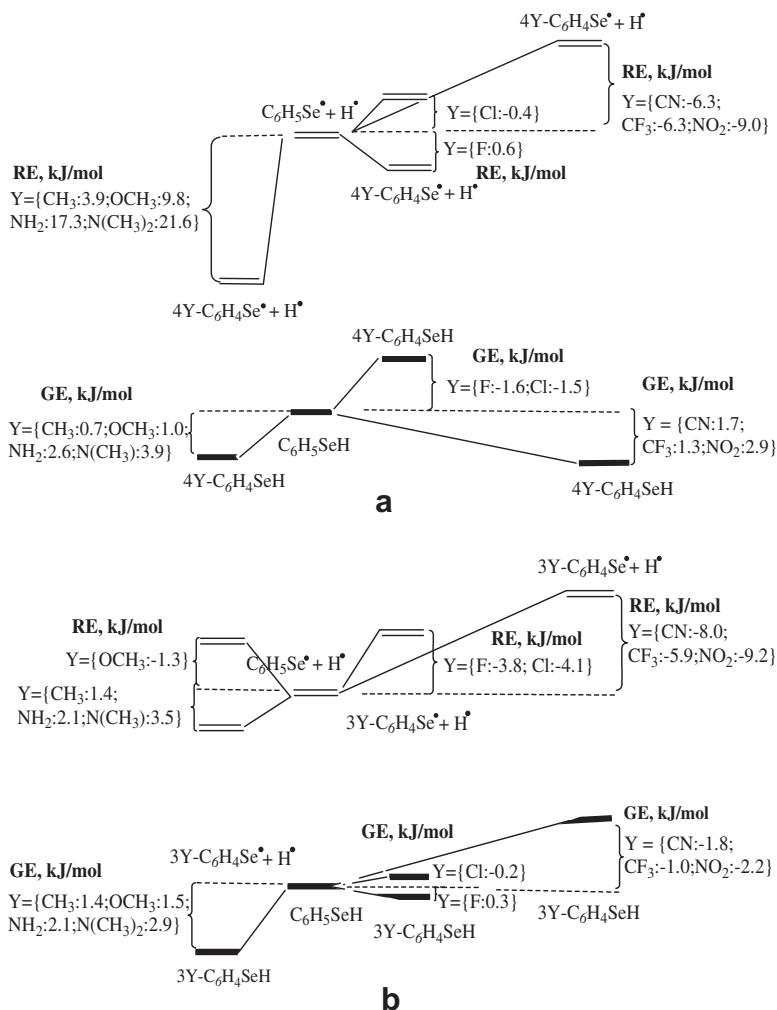
Scheme 2.

and as a result, the BDE(Se–H) is slightly increased. For the ED groups, excluding OCH_3, they stabilize simultaneously both the neutrals and their radicals. The ratios of RE/GE values are approximately equal to 1, therefore, they do seemingly not affect much the TE. The EW groups exert consistent effects on both GE and RE values. All of them destabilize both the parent and radical, but the RE values are larger than the GE ones, in such a way that the TEs are dominated by the RE values. Overall, the BDE(Se–H) value increases owing to a stabilization of the parent benzeneselenol.

3.4. Relationship between BDE(Se–H) and spin density at the selenium center of the radical

The Mulliken atomic spin density (MASD) stands for the difference between the α and β electron densities at a certain position. Table 5 lists the MASD values at the selenium center of both series of $4Y-C_6H_4Se$ and $3Y-C_6H_4Se$ radicals. Again, the trend of change in MASDs by the nature of substituents and their site on the ring turns out to be similar to that of BDE(Se–H) values. For electron-withdrawing groups such as CN, CF_3 and NO_2 located at both *para* and *meta* positions, the MASD at the Se radical center is found to be increased in comparison to that of the parent radical, but this deviation is stronger upon *meta*-substitution. Strong electron donating groups including the CH_3, OCH_3, NH_2 and $N(CH_3)_2$ reduce the MASDs considerably, especially when they are *para*-positioned. A reduced MASD corresponds to a delocalization of the unpaired electron over the benzene ring. The larger the MASD decrease, the stronger the electron delocalization, and as a result the more stable the radical. Therefore, the radical stabilization energies, when breaking the Se–H bond in benzeneselenols, are expected to have a certain relationship with the changes of MASDs at Se center.

To exploit further this point, a relationship between the MASD at Se and the well known Hammett parameters [34] with the BDE(Se–H)'s is searched for and shown in Figs. 2 and 3. For *para*-substituted benzeneselenols, the correlation equations between MASD and Hammett (σ_p) parameters with BDE(Se–H) obtained are given in Eqs. (4a) and (5), respectively. It is interesting to see that a correlation between BDE(Se–H) and MASD is established but not strongly enough ($R^2 = 0.8976$) when the whole set of substituents is taken into account. However this correlation becomes better when only the F, Cl atoms and the electron donating groups are considered in this relationship (Eq. (4b), $R^2 = 0.9953$).

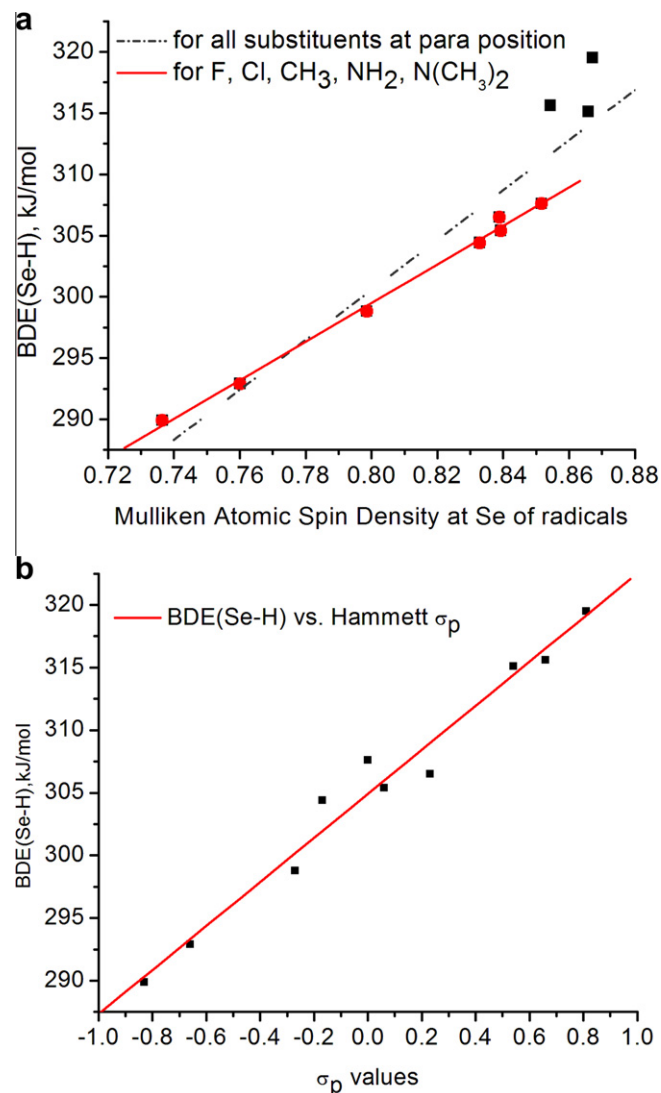$$BDE(Se-H) = 203.82 MASD(Se) + 137.51 (R^2 = 0.8976, \text{ for all substituents})$$
(4a)

Fig. 2. The Mulliken atomic spin density plot (a) and Hammett plot (b) of the BDE(Se–H) values of *para* substituted benzeneselenols.

$$BDE(Se-H) = 157.50 MASD(Se) + 173.48$$
(4b)

$$(R^2 = 0.9953, \text{ for } F, Cl, CH_3, NH_2, N(CH_3)_2)$$

Table 5
Mulliken atomic spin densities (MASD) at the Se center of *para*- and *meta*-substituents using B3LYP functional with the 6-311++G(2df,2p) basis set.

Y	$4Y-C_6H_4SeH$				$3Y-C_6H_4SeH$			
	(U)B3LYP		(RO)B3LYP		(U)B3LYP		(RO)B3LYP	
	$MASD^a (\times10^2)$	$\Delta MASD^b (\times10^2)$	$MASD^a (\times10^2)$	$\Delta MASD^b (\times10^2)$	$MASD^a (\times10^2)$	$\Delta MASD^b (\times10^2)$	$MASD^a (\times10^2)$	$\Delta MASD^b (\times10^2)$
H	85.17	0.00	79.52	0.00	85.17	0.00	79.52	0.00
F	83.93	−1.24	78.23	−1.29	85.92	0.75	80.16	0.64
Cl	83.89	−1.28	78.28	−1.24	86.10	0.93	80.34	0.82
CH_3	83.29	−1.88	77.68	−1.84	84.96	−0.21	78.95	−0.57
OCH_3	79.86	−5.31	74.11	−5.41	85.88	0.71	80.04	0.52
NH_2	76.01	−9.16	70.24	−9.28	83.88	−1.29	78.17	−1.35
$N(CH_3)_2$	73.65	−11.52	67.81	−11.71	83.93	−1.24	77.73	−1.79
CN	85.44	0.27	79.83	0.31	87.39	2.22	81.56	2.04
CF_3	86.59	1.42	81.00	1.48	86.87	1.70	80.97	1.45
NO_2	86.72	1.54	81.07	1.56	87.75	2.58	81.85	2.33

[a] MASD and ΔMASD values are multiplied by 10^2.
[b] ΔMASD = MASD(YC$_6$H$_4$Se•) – MASD(C$_6$H$_5$Se•).
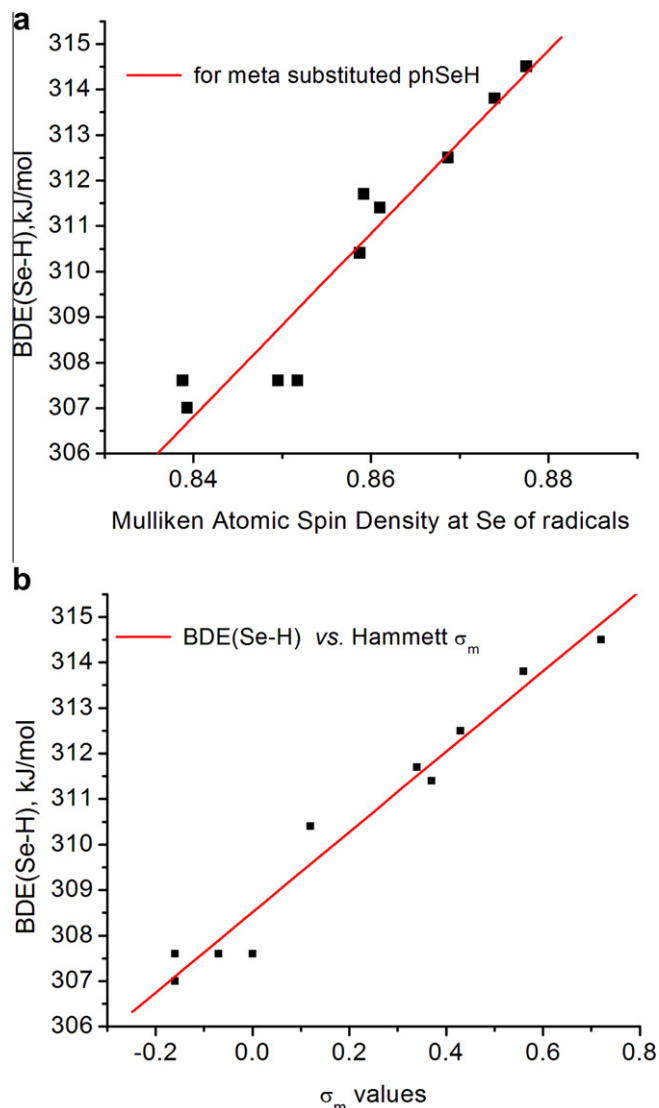
Fig. 3. The Mulliken atomic spin density plot (a) and Hammett plot (b) of the BDE(Se–H) values of *meta* substituted benzeneselenols.

$$BDE(Se{-}H) = 17.587\sigma_p + 304.92 (R^2 = 0.9723) \quad (5)$$

On the other hand, a linear correlation between BDE(Se–H) and MASD(Se) values is better established including all substituents at the *meta* position of the ring with the correlation given in the Eq. (6).

A good linear correlation between the BDE(Se–H)'s of *meta*-Y-C$_6$H$_4$SeH and Hammett parameters is also found as illustrated in Fig. 3b. The correlation obtained in this case is given in Eq. (7):

$$BDE(Se{-}H) = 201.36MASD(Se) + 137.67 (R^2 = 0.9121) \quad (6)$$

$$BDE(Se{-}H) = 8.8162\sigma_m + 308.51 (R^2 = 0.9669) \quad (7)$$

3.5. Ionization energies of substituted benzeneselenols

Ionization energy (IE) is often used to evaluate the antioxidant capacity of a compound based on the electron transfer mechanism. The IEs of benzeneselenol and its derivatives at *para* and *meta* positions are calculated using the B3LYP functional with two basis sets. Calculated results are summarized in Table 6. The calculated adiabatic ionization energy of benzeneselenol amounts to 7.99 eV, which is 0.29 eV larger than the earlier value of Barker and coworkers listed in the NIST Chemistry WebBook [35]. π-donor groups including OCH$_3$, NH$_2$ and N(CH$_3$)$_2$ tend to decrease the IE but more remarkably at the *para* position. Both the π-acceptors (NO$_2$, CN) and σ-acceptor (CF$_3$) increase the IE at both *para* and *meta* positions. The effect of the halogens F and Cl is not significant.

The above trends were previously observed for the case of phenols and thiophenols. For example, when NH$_2$ is attached at the *para* position, the BDE's reductions amount to −22.6 kJ/mol [30] and −40.2 kJ/mol [36] with respect to the parent thiophenol and phenol, respectively.

The values of the BDE(Se–H) and IE listed in Tables 3 and 6 suggest that the amino-substituents NH$_2$ and N(CH$_3$)$_2$ can reduce significantly both parameters especially when they are located at the *para* position. Low BDE and low IE values usually enhance the antioxidant potency [37–41]. Therefore such substituted derivatives can be considered as potentially strong antioxidants.

4. Concluding remarks

In this theoretical study, we find that the parent benzeneselenol exhibits two lowest-energy conformers in which the hydrogen at the Se center is located out of the aromatic ring and has a tendency to freely rotate around the Se–C axis. Calculated proton affinities at the different positions indicate that the preferential site of protonation is the *para* carbon of the ring. The proton affinity and ionization energy of benzeneselenol are evaluated to be PA(C$_6$H$_5$SeH) = 814 ± 4 kJ/mol and IE(C$_6$H$_5$SeH) = 8.0 ± 0.1 eV. The BDE(Se–H) of benzeneselenol is calculated using different functionals whose results are internally consistently but differ much from the available experimental values. There are two lower-lying electronic states of the benzeneselenol radical, namely $^2A'$ and $^2A''$.

Table 6
Calculated ionization energies (IE) for *para*- and *meta*-substituted benzeneselenols (eV) using (U)B3LYP/6-311++G(2df,2p)[a].

Substituent Y	*para* 4Y-C$_6$H$_4$Se-H		*meta* 3Y-C$_6$H$_4$Se-H		ΔIEp−m
	IE	ΔIE[b]	IE	ΔIE[c]	
H	7.99 (7.97)	0.00 (0.00)	7.99 (7.97)	0.00 (0,00)	0.00 (0,00)
F	8.03 (8.01)	0.04 (0.04)	8.21 (8.17)	0.22 (0.20)	−0.18 (−0.16)
Cl	7.97 (7.99)	−0.02 (0.02)	8.17 (8.16)	0.18 (0.19)	−0.20 (−0.17)
CH$_3$	8.34 (8.32)	0.35 (0.35)	8.45 (8.43)	0.46 (0.46)	−0.11 (−0.11)
OCH$_3$	7.40 (7.37)	−0.59 (−0.60)	7.73 (7.69)	−0.26 (−0.28)	−0.33 (−0.32)
NH$_2$	7.06 (7.00)	−0.93 (−0.97)	7.39 (7.32)	−0.60 (−0.65)	−0.33 (−0.32)
N(CH$_3$)$_2$	6.73 (6.69)	−1.26 (−1.28)	7.02 (6.97)	−0.97 (−1.00)	−0.29 (−0.28)
CN	8.45 (8.40)	0.46 (0.43)	8.50 (8.46)	0.51 (0.49)	−0.05 (−0.06)
CF$_3$	8.40 (8.35)	0.41 (0.38)	8.36 (8.31)	0.37 (0.34)	0.04 (0.04)
NO$_2$	8.65 (8.60)	0.66 (0.63)	8.56 (8.52)	0.57 (0.55)	0.09 (0.08)

[a] Results given in parenthesis are calculated at the B3LYP/6-311G(d,p) level.
[b] IE(4Y-C$_6$H$_4$SeH) – IE(C$_6$H$_5$SeH).
[c] IE(3Y-C$_6$H$_4$SeH) – IE(C$_6$H$_5$SeH).

The BDE related to the ground $^2A''$ electronic state of benzeneselenol radical is predicted to be BDE(Se–H) = 308 ± 8 kJ/mol (73.6 ± 2 kcal/mol).

We determine the BDE(Se–H) values for a series of derivatives having substituents at both *para* and *meta* positions. The spin densities at the selenium radical center are found to have a correlationship with the changes of BDE(Se–H) values in the case of *para* substitution by F, Cl, CH_3, OCH_3, NH_2, $N(CH_3)_2$. With π-donor groups such as NH_2, $N(CH_3)_2$ and OCH_3 at the *para* position of the ring, the BDE(Se–H) is decreased significantly. Good correlations are also observed between BDE(Se–H) values and Hammett's parameters. Ionization energies for the *para* and *meta* substituted derivatives are also evaluated. This shows that the IE of $N(CH_3)_2$-C_6H_4SeH is markedly reduced in both positions. On the basis of the calculated results, we would suggest that the 4-amino-benzeneselenol derivatives can be considered as efficient antioxidants.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2013.02.008.

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