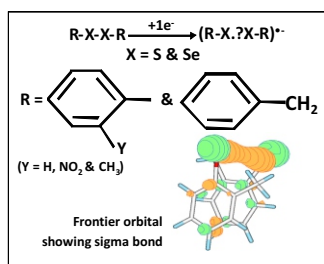


Density Functional Theory

9

Effect of Excess Electron on Structure and Properties of Diphenyldichalcogen Systems

Dilip Kumar Maity^{1,2}¹Director's Office, Bhabha Atomic Research Centre (BARC), Trombay-400085, INDIA²Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, INDIA

ABSTRACT

Ab initio quantum chemical methods are employed to elucidate structure and properties of sulfur and selenium based dichalcogen systems of the type $(R-X)_2$ ($R=Ph, PhCH_2$; $X=S, Se$) in presence of an excess electron. Effect of electron withdrawing ($-NO_2$) and electron donating ($-CH_3$) groups in phenyl ring on the stability of these two-center three-electron (2c-3e) bonded systems in water medium is discussed. This report illustrates that the combination of electronic effect and geometrical flexibility decides the strength of 2c-3e bond in these systems and this study also helps to understand antioxidant properties of anionic dichalcogen systems.

KEYWORDS: Antioxidant, Chalcogen, Radical anion, Structure and properties

Introduction

Sulfur and selenium based diaryldichalcogenes are eco-friendly oxidizing agents and important drugs in pharmaceutical industry mainly due to their antioxidant properties [1]. One electron reduction of neutral disulfides and diselenides may lead to the formation of two-center three-electron (2c-3e) bonded radical anion systems [2]. The extra electron in such systems is accommodated in the lowest unoccupied molecular orbital which is often an antibonding sigma orbital. Due to the presence of this electron in a repulsive antibonding orbital, such three electron bonded species are not very stable and may dissociate easily. Electron capture dissociation (ECD) with Fourier transform ion cyclotron mass spectrometry (FTICR MS) has been used for direct measurement of sulfur and selenium centered 2c-3e bonded complexes [3]. Areal time probing of 2c-3e bonded sulfur system has also been performed following femtosecond laser spectroscopy. Recently, transient anion states of gas-phase diphenyldisulfide are characterized by means of electron transmission (ET) and dissociative electron attachment (DEA) spectroscopic methods. Quantum chemical calculations play a major role in understanding the nature of this type of three electron bonding. Mixing of two sulfur valence p-orbitals from the respective radical anion, RS^- and free radical, RS form disulfide radical anion ($(R-S)_{2\cdot}$ or $(R-S)^{\cdot-}$) having a three electron bond between two sulfur atoms. Bond strength of such a bond is expected to depend on the combined effects of structural parameters, substitution patterns and electronic interactions. The combined effects are expected to control the extent of p-orbital interaction that in turn is expected to influence the strength of the newly formed bond.

Over the years several chalcogen based radical cation and anion systems are studied applying theoretical and pulse radiolysis based experimental techniques to understand

nature of bonding and antioxidant properties. At present, electron acceptor properties of dichalcogen systems, namely, diphenyldisulfide and diphenyldiselenide of the type $R-X-X-R$ ($X=S, Se$; $R=Ph, PhCH_2$) are discussed and the newly formed 2c-3e bonds in their anionic $(R-X-X-R)^{\cdot-}$ states are characterized as a case study. These are model systems for understanding the antioxidant behavior of sulfur and selenium based biological systems.

Computational Methods

First principle based quantum chemical calculations are performed to find out the most stable structure of different $(Ph-X-X-Ph)^{\cdot-}$ radical anion systems under gas phase isolated condition. Further optimization of such geometries is carried out including solvent effects following a macroscopic solvation model following SMD model in water medium. To calculate geometrical and energy parameters of these systems, a long range corrected DFT functional including dispersion correction (ω -B97XD) and MP2 method are employed along with 6-311++G(d,p) set of atomic basis functions. Restricted Open Shell HartreeFock (ROHF) formalism is applied to avoid any spin contamination in these doublet radical anionic systems.

Results and Discussion

Structure & Stability of $(R-S)_2$ and $(R-S)_2^{\cdot-}$ ($R=Ph, PhCH_2$)

Two minimum energy equilibrium structures are obtained for neutral diphenyldisulfide system and these structures differ mainly in spatial orientation of two phenyl rings. To calculate gas phase geometrical parameters of $(PhS)_2$ system more accurately, geometry optimization is also carried out at CCSD level of theory which is known to recover dynamic correlation accurately. Geometrical parameters of neutral $(PhS)_2$ and $(PhCH_2S)_2$ calculated at ω -B97XD/6-311++G(d,p) level agrees well with that obtained at MP2 as well as CCSD level of theory. Geometry of the most stable structures are recalculated in water medium applying a continuum model for

*Author for Correspondence: Dilip Kumar Maity
E-mail: dkmaity@barc.gov.in

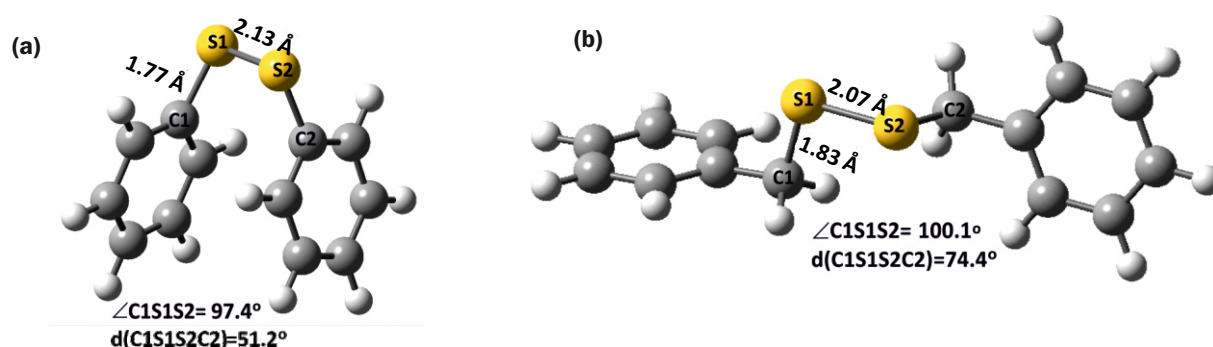


Fig.1: Most stable equilibrium structure of (a) $(PhS)_2$ and (b) $(PhCH_2S)_2$ systems calculated at MP2/6-311++G(d,p) level in water medium. Selected bond lengths, bond angle and dihedral angle are also shown.

hydration. Most stable structures of $(PhS)_2$ and $(PhCH_2S)_2$ calculated at MP2 level in water medium are provided in Fig.1 (a-b). In case of the most stable structure of $(PhCH_2S)_2$ system, two benzyl rings are in anti-position as can be seen from the figure. Table 1 summarizes the changes in selected geometrical parameters and molecular properties of $(PhS)_2$ and $(PhCH_2S)_2$ systems produced upon capture of an electron.

Two minimum energy structures are obtained for diphenyldisulfide, $(PhS)_2$ and the two structures differ mainly in spatial orientation of two phenyl rings. In the first case, one phenyl ring is displaced over the other phenyl ring and due to partial interactions of pi orbitals from two phenyl rings, the first structure is more stable than the second one by 3.8 kcal/mol at MP2 level. Calculated S1-S2 and C1-S1 bond distances are 2.87 Å and 1.77 Å respectively and these are very close to MP2 values. The respective bond angle, $\angle C1S1S2$, dihedral angles, $\delta(C1S1S2C2)$, $\delta(S1S2C2C2')$ and $\delta(S2S1C1C1')$ are predicted as 91.6° , 41.8° and 78.8° and -99.8° . Calculated distances C1-C2 and C3-C4 at MP2 level (see Fig.2 (a) for atom labels) are 3.0 Å and 4.4 Å respectively. Respective bond distances S1-S2 and C1-S1 are 2.82 Å and 1.77 Å and the bond angle, $\angle C1S1S2$ and dihedral angle, $\delta(C1S1S2C2)$ are 87.7° and 49.5° respectively in water medium. The distance between C1 and C2 atoms 3.0 Å and the same between C3 and C4 atoms is 4.4 Å. Calculated dipole moments are 7.24 D and 10.97 D in the gas phase and water medium respectively. Thus, MP2 results on geometrical parameters suggest that on attachment of an excess electron, the dichalcogen bond, S1-S2 elongates by 0.7 Å and C1-S1 bond distance remains practically unchanged in the gas phase and in water medium for $(PhS)_2$ system. Along with that, bond angle ($\angle C1S1S2$) and dihedral angle, $\delta(C1S1S2C2)$ remain unperturbed on electron attachment in $(PhS)_2$ in the gas phase as well as in water medium.

Now a $-CH_2-$ group is added to the structure of radical anion $(PhS)_2^-$ between each phenyl ring and the chalcogen S atom to provide molecular flexibility and the calculations are carried out for $(PhCH_2S)_2^-$ radical anion. Optimized structures are different than those of diphenyl disulfide radical anion. Calculated S1-S2 and C1-S1 bond distances are 2.76 and 1.82 Å respectively. It may be noted that S1-S2 bond is shorter in $(PhCH_2S)_2^-$ by 0.07 Å than that in $(PhS)_2^-$. The obtained bond angle, $\angle C1S1S2$ and dihedral angle, $\delta(C1S1S2C2)$ are 90.5° and 71.8° respectively (see Fig.2 (b) for atom labels). The distance between the two phenyl rings and their orientations do not allow any pi-pi interactions. The dipole moment of this radical anionic system is calculated as 7.3 D. The other equilibrium structure having all anti-structure and is less stable than the most stable one by 8.6 kcal/mol.

It is observed that sulfur atoms are more negative in water medium than in gas phase for both the radical anions. It may be noted that the calculated bond order between two S atoms is close to 0.5 in these negatively charged systems. The odd electron spin is observed to be equally localized on two S atoms. On addition of an excess electron to $(PhS)_2$, the distance between two sulfur atoms is increased by 25% and binding energy is decreased by 57% as compared to the neutral counterpart, $(PhS)_2$ at MP2 level. Electron affinity (adiabatic) of $(PhS)_2$ is -0.7 eV in gas phase and the same in water medium is -2.5 eV. This suggests that the excess electron can easily bound to the system in water medium. It is noted that calculated binding energy of $(PhS)_2$ is reduced by 7.8 kcal/mol in water medium compared to the same in gas phase. This indicates that solvents play a significant role on the stability of these systems having an excess electron. In water medium, with respect to neutral $(PhS)_2$ system, the distance between two sulfur atoms is calculated to be increased by 24% and binding energy is decreased by 70% when an extra electron is

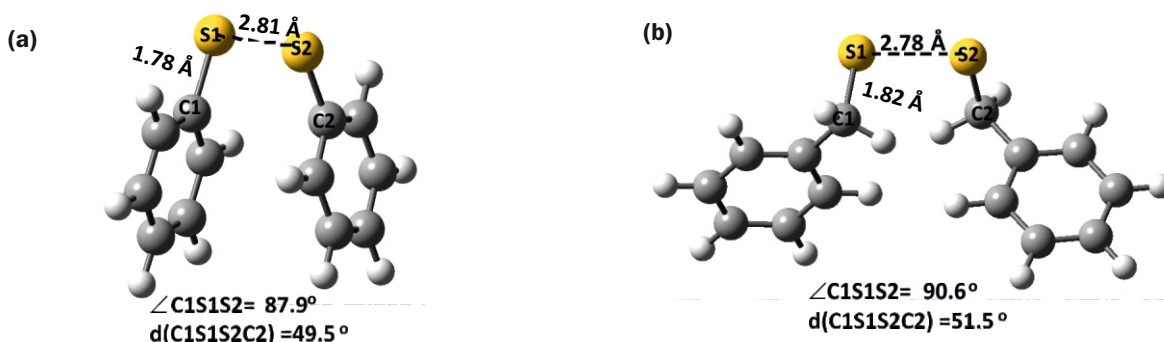


Fig.2: Most stable equilibrium structure of (a) $(PhS)_2$ and (b) $(PhCH_2S)_2$ systems calculated at MP2/6-311++G(d,p) level in water medium. Selected bond lengths, bond angle and dihedral angle are also shown.

Table 1: Selected geometrical and molecular parameters of $(R-X)_2$ in water medium calculated at MP2/6-311++G(d,p) level of theory. Values in the braces show the parameters in presence of an excess electron, $(R-X)_2^-$ ($R=Ph, PhCH_2, o-NO_2Ph, o-CH_3Ph; X=S, Se$).

r_{X1X2} (Å)	r_{C1X1} (Å)	$\angle C1X1X2$ (degree)	$d(C1X1X2C2)$ (degree)	$d(X1X2C2C2')$ (degree)	$d(X2X1C1C1')$ (degree)	Atomic charge on Sulfur (a.u.)	Electron Affinity (eV)	Binding Energy (kcal/mol)
diphenyldisulfide, $(PhS)_2$								
2.13, (2.81)	1.77, (1.76)	97.6, (88.0)	47.7, (49.5)	74.5, (70.1)	-101.7, (-110.9)	-0.49, (-0.91)	-2.5	68.8, (20.5)
dibenzyl disulfide, $(PhCH_2S)_2$								
2.07, (2.78)	1.82, (1.82)	100.7, (90.6)	81.1, (71.7)	-178.0, (-141.6)	-177.9, (-141.6)	-0.34, (-0.83)	-2.3	61.6, (16.3)
diphenyldiselenide, $(PhSe)_2$								
2.41, (3.05)	1.92, (1.92)	94.7, (92.4)	42.3, (22.8)	73.7, (47.3)	-102.6, (-131.7)	-0.20, (-0.54)	-3.0	92.4, (23.2)
dibenzyl diselenide, $(PhCH_2Se)_2$								
2.35, (2.97)	1.98, (1.99)	99.3, (90.0)	81.1, (69.7)	-177.1, (-133.6)	-177.1, (-133.4)	-0.20, (-0.70)	-2.7	61.7, (21.1)
ortho-nitro-diphenyldiselenide, $(o-NO_2-PhSe)_2$								
2.40, (2.41)	1.93, (1.92)	97.2, (95.3)	34.0, (37.7)	49.6, (75.1)	-123.1, (-101.1)	-0.09, (-0.10)	-2.9	60.7, (21.0)
ortho-methyl-diphenyldiselenide, $(o-CH_3-PhSe)_2$								
2.41, (3.03)	1.92, (1.94)	96.6, (87.9)	37.8, (40.0)	77.0, (77.1)	-99.9, (-105.3)	-0.22, (-0.55)	-3.0	94.9, (26.5)

added to the system. The binding energy of dibenzyl disulfide radical anion is calculated to be lower by 4.2 kcal/mol compared to that in $(PhS)_2$, S1-S2 distance is shorter by 0.05 Å though. This indicates that geometrical flexibility incorporated by adding a $-CH_2-$ group does not play any significant role to stabilize these radical anions and electronic effects are expected to play a major role to stabilize/destabilize these systems.

Structure & Stability $(R-Se)_2$

$(R=Ph, PhCH_2, o-CH_3Ph, o-NO_2Ph)$

Calculated geometrical parameters of the most stable structures of $(PhSe)_2$ and $(PhCH_2Se)_2$ systems in presence of an excess electron are provided in Table 1. Two minimum energy structures are also obtained in these systems similar to diphenyldisulfide system discussed before. Such observations are also reported in the literature for diphenylchalcogen systems including $(PhTe)_2$ based on conformation analysis. On geometry optimization, two equilibrium structures are obtained for diphenyldiselenide radical anion and the most stable structure obtained in water medium is displayed in Fig.3(a) along with selected geometrical parameters. One can see that one phenyl ring is displaced over the other phenyl ring to a lesser extent compared to the most stable structure of diphenyldisulfide radical anion. The most stable structure is

more stable than the second equilibrium structure by 9.4 kcal/mol. This extra stability may be attributed to pi orbital interactions from two phenyl rings. Calculated gas phase Se1-Se2 and C1-Se1 bond distances 3.04 Å and 1.92 Å respectively and are longer than the sulfur system as expected. Bond angle, C1Se1Se2 and dihedral angle, $\delta(C1Se1Se2C2)$ are predicted as 92.2° and 28.2° respectively. It may be noted that calculated dihedral angle, $\delta(C1Se1Se2C2)$ is significantly smaller than the sulfur systems suggesting more pi-pi interaction in Se systems. The Se1-Se2 and C1-Se1 bond distances are 3.03 Å and 1.93 Å respectively in water medium showing no significant effect of solvent water medium. The obtained bond angle, $\angle C1Se1Se2$ and dihedral angle, $\delta(C1Se1Se2C2)$ are 92.4° and 21.2° respectively in water medium. Calculated dihedral angle suggests that two phenyl rings in the radical anion, $(PhSe)_2^-$ become less displaced in water environment. The distance between the C1 and C2 atoms is 3.3 Å and that between C3 and C4 atoms is 3.8 Å. Calculated dipole moments are 5.6 D and 10.7 D in the gas phase and water medium respectively. When a $-CH_2-$ group is added between each phenyl ring and Se atom to the structure of radical anion $(PhSe)_2^-$, again only two stable equilibrium structures are obtained. These structures are very different from those of $(PhSe)_2^-$. One structure is more stable than the other one by 9.1 kcal/mol. Structure and selected geometrical

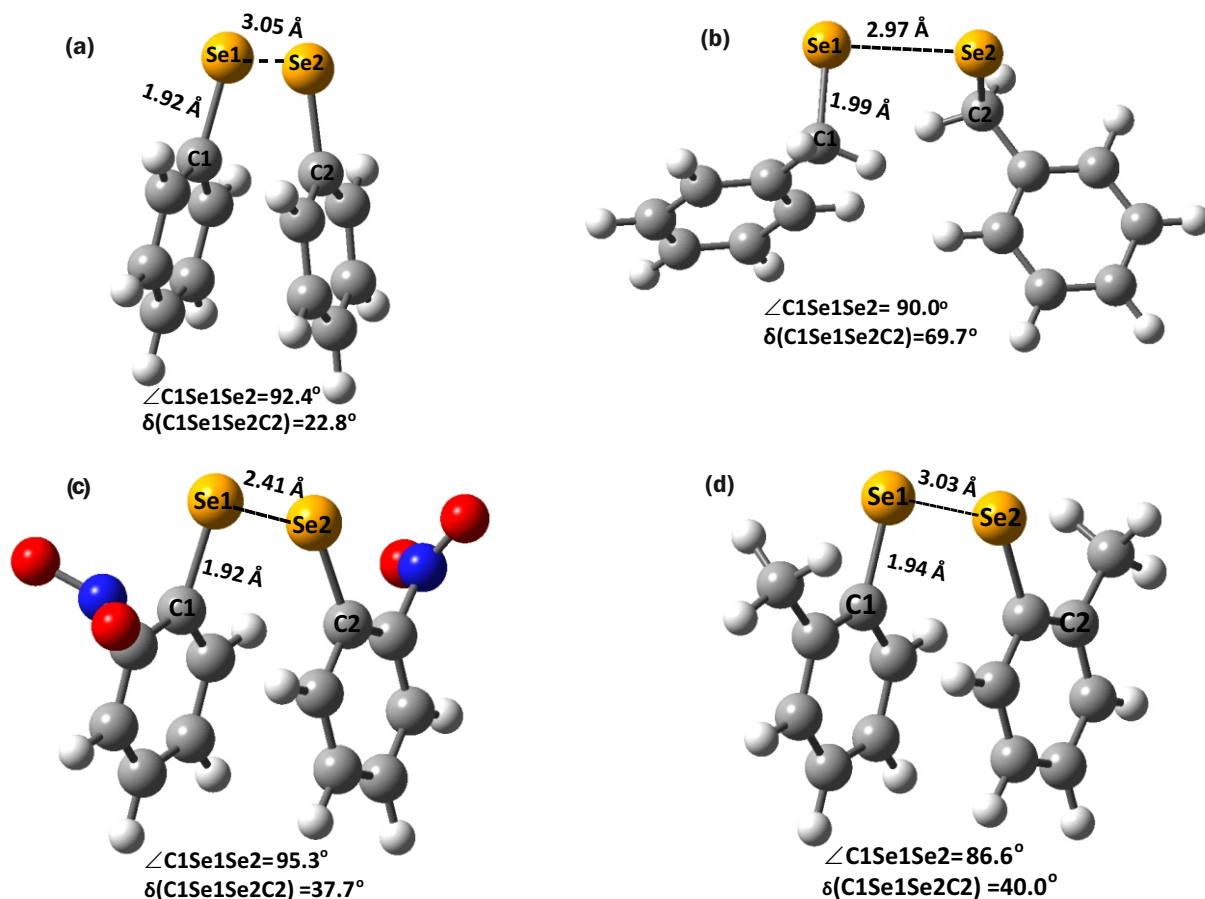


Fig.3: Most stable equilibrium structure of (a) $(\text{PhSe})_2$, (b) $(\text{PhCH}_2\text{Se})_2$, (c) $(o\text{-NO}_2\text{PhSe})_2$ and (d) $(o\text{-CH}_3\text{PhSe})_2$ systems calculated at MP2/6-311++G(d,p) level in water medium. Selected bond lengths, bond angle and dihedral angle are also shown.

parameters of the most stable one as calculated in water medium is given in Fig.3 (b). Calculated Se1-Se2 and C1-Se1 bond distances are 3.10 and 2.01 Å respectively. It may be noted that Se1-Se2 bond is longer in $(\text{PhCH}_2\text{Se})_2$ by 0.07 Å than that in $(\text{PhSe})_2$ in contrast to its sulfur counterpart. The obtained bond angle, $\angle\text{C1Se1Se2}$ and dihedral angle, $\delta(\text{C1Se1Se2C2})$ are 93.9° and 78.8° respectively. Calculated data suggests that on the addition of $-\text{CH}_2-$ group, molecular geometry and properties are similar to corresponding S system. The dipole moment of this dimer radical anionic system is calculated as 12.7 D.

Effect of electron withdrawing/donating group on structure and stability of the radical anion, $(\text{PhSe})_2$ is also studied by substituting one of the ortho- positions of the two phenyl rings. Structures with $-\text{NO}_2$ and $-\text{CH}_3$ substitutions only in anti-positions of the most stable structure of diphenylselenide radical anion are considered as input geometries to locate equilibrium structure. The most stable structure of $(o\text{-NO}_2\text{PhSe})_2$ radical anion along with certain geometrical parameters is shown in Fig.3 (c). It is interesting to note that adding an electron withdrawing group like $-\text{NO}_2$ to each phenyl ring in their ortho position has made the distance between two Se atoms shorter by 0.64 Å in water medium. However, dihedral angle, $\delta(\text{C1Se1Se2C2})$ is increased by 15.8 degree indicating less pi-pi interaction. On addition of an electron donating group like $-\text{CH}_3$ to the phenyl ring, no notable change in the distance between two Se atoms is obtained and the structure is displayed in Fig.3 (d). However, dihedral angle, $\delta(\text{C1Se1Se2C2})$ is increased by 18° compared to that in the radical anion with unsubstituted phenyl rings. This increase in dihedral angle reflects the displacement between the two phenyl rings may be due to bulky nature of $-\text{NO}_2$ and $-\text{CH}_3$ groups.

In short, the structures obtained for radical anions of $(o\text{-CH}_3\text{-PhSe})_2$ and $(o\text{-NO}_2\text{-PhSe})_2$ are very similar to the parent radical anion. The binding energy of $(\text{PhSe})_2$ radical anion with respect to its dissociative products PhSe and PhSe is calculated as 34.2 kcal/mol. The calculated increase in the distance between two selenium atoms in the radical anion is 21% and decrease in binding energy is 63% as compared to the neutral system, $(\text{PhSe})_2$. Binding energy of $(\text{PhSe})_2$ is significantly smaller in water medium compared to the gas phase data (see Table 1). On substituting by $-\text{CH}_3$ group at ortho position of the phenyl rings, binding energy of the radical anion is increased by 3.3 kcal/mol compared to the unsubstituted radical anion, $(\text{PhSe})_2$. However, in case of $(o\text{-NO}_2\text{-PhSe})_2$ system, binding energy is decreased by 2.2 kcal/mol, the distance between the two Se atoms is reduced significantly though. Thus, substitution by an electron withdrawing group in the phenyl ring decreases the stability of $(\text{PhSe})_2$ showing strong electronic effect in the binding characteristics of these hemi bonded systems. Calculated atomic charges do support this observation. Though in case of $(o\text{-CH}_3\text{-PhSe})_2$ system, odd electron spin is equally localized over two Se atoms; for $(o\text{-NO}_2\text{-PhSe})_2$ system, the odd electron spin is not localized over Se atoms.

Visualization of selected molecular orbitals in these radical anions is important to understand the nature of bonding features. Selected molecular orbitals involved in electronic transition of the major optical band of these radical anion systems are visualized. These orbitals are based on the most stable structures of the radical anions in water medium and involved in the most prominent electronic transitions in the visible region [4]. It is clearly seen that in case the highest doubly occupied orbitalexcept for $(o\text{-NO}_2\text{-PhSe})_2$, two p-orbitals from two sulfur/selenium atoms of these radical anion mixes head-on showing the presence of a bonding sigma (σ) orbital. In

case of the lowest singly occupied orbital, two p-orbitals having opposite symmetry are orientated towards each other indicating the presence of an anti-bonding sigma (σ^*) orbital. Thus, the optical absorption band obtained in these radical anion systems are due to $\sigma \rightarrow \sigma^*$ transition as known to occur in a *two-centre three-electron* bonded system. In case of $(\text{PhSe})_2$ system, a better mixing of the two p-orbitals from two Se atoms is observed.

Conclusion

The effect of an excess electron on geometry, nature of bonding and stability of diaryldichalconides, namely, $(\text{PhS})_2$, $(\text{PhSe})_2$, $(\text{PhCH}_2\text{Se})_2$, $(o\text{-NO}_2\text{-PhSe})_2$ and $(o\text{-CH}_3\text{-PhSe})_2$ is studied. These dichalcogens have high electron affinity in water medium and should be able to capture electron efficiently suggesting their antioxidant property. It is shown that in presence of an excess electron, these diaryldichalcogen systems are bound by *two-centre three-electron* bond between two chalcogen (S/Se) atoms. Visualization of frontier molecular orbital of the most stable equilibrium structures suggests that sulfur and selenium valence p-orbitals are mixed head-on indicating sigma character of the three electron bond between two S/Se atoms in these radical anions. Atomic spin

populations are equally distributed over two S or Se atoms in these systems except for $(o\text{-NO}_2\text{-PhSe})_2$. Solvent water medium induces red shifts in absorption maxima of these systems with excess electron when solvent effect is introduced through a macroscopic model. The origin of the strong absorption bands in the visible region are assigned to be electronic transition from sigma bonding orbital to antibonding sigma* orbital.

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