

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244272313>

Intramolecular nonbonding interactions in organoseleniums: Quantification using a computational thermochemical approach

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE THEOCHEM · MAY 2007

Impact Factor: 1.37 · DOI: 10.1016/j.theochem.2007.01.022

CITATIONS

5

READS

15

2 AUTHORS:



Dipankar Roy

City University of New York - Hunter College

17 PUBLICATIONS 452 CITATIONS

SEE PROFILE



Raghavan B Sunoj

Indian Institute of Technology Bombay

117 PUBLICATIONS 2,183 CITATIONS

SEE PROFILE

Intramolecular nonbonding interactions in organoseleniums: Quantification using a computational thermochemical approach

Dipankar Roy, Raghavan B. Sunoj *

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

Abstract

Intramolecular Se··O nonbonding interactions in a series of *ortho*-formylarylselenides (O··Se-Y, with Y = -Me, -Ph, -CN, -Cl, and -F) are quantified using density functional theory. Two methods based on the relative stabilities of various conformers are employed in evaluating the strength of intramolecular interactions. These methods, namely, cis-trans (CT) and thermodynamic cycle (TDC), depends on the energy changes associated with conformational interconversion, where the nonbonding interaction is turned *on* or *off* (respectively, in cis and trans conformer). The strength of interactions are found to be dependent on the nature of Se-Y acceptor orbitals and follows the order Me ~ Ph < CN < Cl < F. Natural Bond Orbital (NBO) analysis using DFT methods points to $n_O \rightarrow \sigma_{\text{Se-Y}}^*$ electron delocalization as the key contributing factor towards Se··O nonbonding interaction. Examination of the topological properties of the electron density with the Atoms-in-Molecule (AIM) method reveals that the electron density at the Se··O bond critical point exhibits a fairly good correlation with the nonbonding interaction energies estimated using the CT and TDC methods.

Keywords: Nonbonding interaction; Ab initio calculations; Density functional calculations; Thermochemical cycle; Atoms-in-Molecule; Organoselenium compounds

1. Introduction

The importance of nonbonding interactions has been widely recognized in chemistry, biology, and material science. Some of the popular examples of nonbonding interactions include van der Waals interactions, hydrogen bonding, π -stacking and so on [1–9]. Nonbonding interactions involving a divalent selenium and sulfur atom has received immense attention in recent times owing to their importance in biological activities of certain organoselenium/tellurium compounds, particularly as enzyme mimetic [10–17]. A number of organochalcogen compounds, such as selenazafurin has found interesting applications as anti-inflammatory drugs [18].

Presence of weak intramolecular nonbonding interaction in organochalcogens has been unambiguously demonstrated by using distance criteria, wherein, short Se··X (X = chalcogens, oxygen, nitrogen, halogen etc.) distances determined using X-ray crystallographic techniques are used as an evidence for the existence of strong/weak nonbonding interactions in a large number of organochalcogens [19–32]. When the distance between a pair of interacting atoms falls below the sum of their respective van der Waals radii, nonbonding interaction is said to be operating. It has been proposed that nonbonding electrons on the donor center (such as the O/N/Halogens) delocalize into suitably aligned acceptor antibonding σ^* orbital [26,27]. Thus, the strength of such interaction depends on the ability of donor atoms as well as on how good the acceptor orbital are. In other words, a stronger interaction implies energetically closer disposition of donor-acceptor orbitals and enhanced overlap between them.

While the importance of intramolecular nonbonding interactions in organochalcogens is well recognized, attempts towards quantifying such weak interactions are conspicuously lacking. There are only two rare instances of experimental quantification of nonbonding interactions in organochalcogens. Tomoda and co-workers have employed variable temperature NMR experiments in studying $\text{Se} \cdots \text{F}$ and $\text{Se} \cdots \text{N}$ intramolecular interactions [20,28]. Knowledge on how strong/weak these intramolecular interactions are will be quite valuable as these interactions are proposed to correlate with the enzyme mimetic activities [13,33–36]. The first systematic study towards quantifying intramolecular nonbonding interactions in organochalcogens was reported very recently from our laboratory [37]. Quantum chemical methods in conjunction with a *homodesmotic reaction* scheme and *ortho–para* approaches were employed in estimating intramolecular interactions in a series of ortho substituted arylselenides (Fig. 1). In this report two new approaches for the quantification of intramolecular $\text{Se} \cdots \text{X}$ nonbonding interaction are described. These methods are primarily based on differences and changes in energies associated, respectively, with conformers and conformational interconversion of organoselenium systems.

2. Methods for calculating intramolecular interaction

2.1. Cis–trans (CT) method

In our previous study on related organochalcogen systems, it has been established that in the lowest energy conformer of compounds **1** through **5**, the formyl oxygen remains syn to the Se–Y bond as shown in Fig. 1 [31,32,37]. The anti conformer where the formyl hydrogen is syn to the Se–Y bond is generally found to be higher in energy. Preference for the syn arrangement primarily arises due to the $\text{Se} \cdots \text{O}$ nonbonding interaction. The nonbonding interaction can be thought of as being turned *on* and *off*, respectively, in syn and anti conformations. Thus, the strength of $\text{Se} \cdots \text{X}$ nonbonding interaction can be estimated as the difference in energies between syn and anti conformers. A number of similar approaches have earlier been used in evaluating the strength of intramolecular hydrogen bonding interactions [38–40]. The method referred to as the cis–trans method considers two conformational isomeric forms of the same molecule, cis (**C**) and trans (**T**) as depicted in Scheme 1. Evidently,

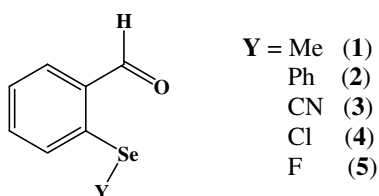
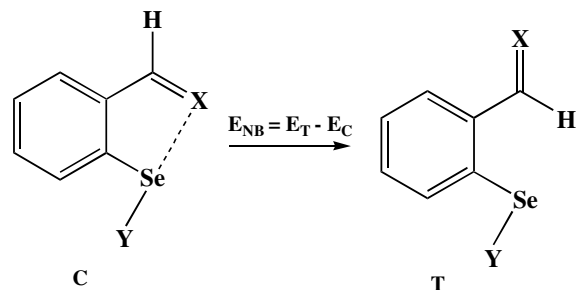


Fig. 1. Organochalcogens considered in this work.



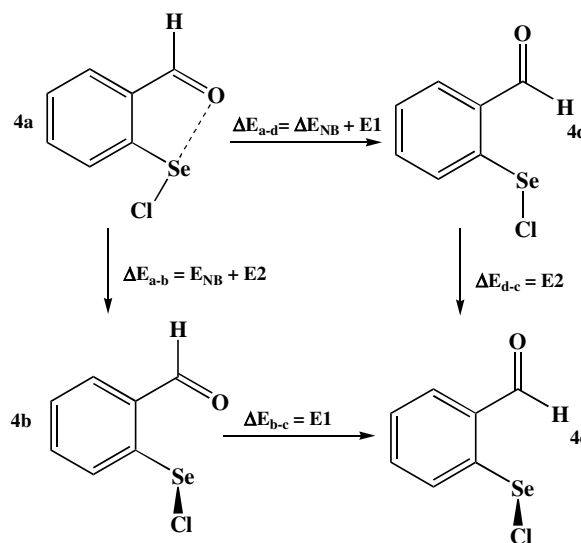
Scheme 1. Cis–trans method for quantification of intramolecular non-bonding interaction.

conformer **C** enjoys additional stabilization due to weak intramolecular nonbonding interaction, whereas in conformer **T**, the donor **X** atom is pointed away from the **Se**.

2.2. Thermodynamic cycle (TDC) method

The cis–trans method can further be refined by incorporating the energies of different conformers in a thermodynamic cycle. Four different conformers of each compound is separately optimized so as to enable us to set-up a thermodynamic cycle based on these conformers as summarized in Scheme 2. The energy changes associated with the transformation, in which a closed-conformer (the one with nonbonding interaction *on*) converts to an open-conformer (conformer with nonbonded interaction *off*), is determined [41].

The thermodynamic cycle can be briefly illustrated with the help of Scheme 2 by choosing compound **4** as an example. In conformers **4b** and **4c**, the Se–Cl bond is orthogonal to the aryl ring while **4a** and **4d** have a plane of symmetry. In **4b** and **4c**, since the acceptor orbital $\sigma_{\text{Se–Y}}^*$ is aligned orthogonal to the aryl ring; $\text{Se} \cdots \text{X}$ nonbonding interaction



Scheme 2. Proposed thermodynamic cycle based on conformational changes towards quantifying nonbonding interaction.

arising due to orbital interaction will be absent. In such a situation, the difference in enthalpy between **4a** and **4d** (ΔE_{a-d}) can be described as a quantity comprising of the intramolecular nonbonding interaction (E_{NB}) and an energy term (E1) associated with the change in orientation of the formyl oxygen away from selenium atom. Similarly, the difference in enthalpy between **4b** and **4a** (ΔE_{a-b}) consists of intramolecular nonbonding interaction and an energy term (E2) associated change in orientation of the Se–Y bond with respect to the aryl ring. Furthermore, the enthalpy difference between **4d** and **4c** (ΔE_{d-c}) relates to the change in environment around the selenium atom due to the rotation of the Y group. The same is true for the enthalpy difference between **4b** and **4c** (ΔE_{b-c}). Thus, the enthalpy terms associated in the thermodynamic cycle can reasonably be expressed as: $\Delta E_{a-d} = E_{NB} + E1$; $\Delta E_{a-b} = E_{NB} + E2$; $\Delta E_{d-c} = E2$; $\Delta E_{b-c} = E1$. Evidently, the difference between ΔE_{a-d} and ΔE_{b-c} is the nonbonding interaction energy. The same argument holds for the difference between ΔE_{a-b} and ΔE_{d-c} .

3. Computational methods

All calculations were performed with the Gaussian98 and Gaussian03 quantum chemical programs [42,43]. Full geometry optimizations without any geometry constraint and frequency calculations on all the stationary points were carried out using the density functional theories with the B3LYP and BHandHLYP functionals [44–46]. Dunning's correlation consistent basis set of double zeta quality, namely, cc-pVDZ was used for all these calculations [47,48]. Use of hybrid Hartree–Fock DFT methods have been recommended for studies on intramolecular hydrogen bonded systems [49–58]. The successful applications of B3LYP functional in chemical reactivity problem as well as in studying weak interaction is documented well in literature [59–63]. We therefore decided to apply this hybrid DFT functional in quantifying intramolecular interaction. Further, BHandHLYP functional is known to address weak interactions reasonably well [64–66]. Nonbonding interaction energy (E_{NB}) is calculated as the heat of reaction $\Delta H_{298\text{ K}}$ associated with conformational interconversion as shown in the quantification schemes i.e., $\Delta H_{298\text{ K}} = \sum \Delta H_{298\text{ K}}(\text{Product}) - \sum \Delta H_{298\text{ K}}(\text{Reactant})$ (vide

infra). Unless otherwise stated, E_{NB} refers to enthalpies at 298 K.

The general belief that the density functional theories may not be adequate to represent weak interactions, particularly reproducing the correct energetics of van der Waals complexes, prompted us to compare the calculated numbers with the corresponding values obtained at the MP2 level of theory. Cremer and co-workers have shown that hybrid functionals such as the B3LYP could mimic pair and three-electron correlation effects as given by higher level correlated levels such as the coupled cluster methods (CCSD) [67]. Nonbonding interactions in variety of organochalcogens have been extensively studied using the DFT based methods [27–30,68–70]. The excellent concurrence between DFT and MP2 result for a range of intermolecular interactions are also known [71].

The orbital interaction energies between donor–acceptor orbitals, NPA atomic charges, were calculated using the natural bond orbital (NBO) analysis [72,73]. Wiberg bond orders were also evaluated. Topological properties of the electron density (ρ) at the bond critical points for the Se···O interactions were evaluated using the Atoms-in-Molecule (AIM) method with AIM2000 program [74,75]. All these analysis were performed using the same combination of density functionals and basis set.

4. Results and discussion

In ortho formyl substituted arylselenides, the lowest energy conformer has earlier been shown to be the one with formyl oxygen syn to the selenium atom. The anti orientation is found to be 3.21 kcal mol^{−1} higher in energy as compared to the syn conformer at the B3LYP/6-31G* level [31]. Greater preference for the intramolecular Se···O interaction over the likely Se···H interaction, have been found to be the key reason behind such conformational preferences. However, a more appealing question is on the strength of such intramolecular weak interactions.

In this study we have employed two methods towards quantifying weak intramolecular interactions based on a thermochemical cycle. Calculated nonbonding interaction energies (E_{NB}) are summarized in Table 1. It can be easily noticed that the interaction energies are quite sensitive to the nature of acceptor bond (Se–Y). When Y is alkyl or

Table 1

Nonbonding interaction energies (in kcal mol^{−1})^a calculated using four different methods at the L1 (B3LYP) and L2 (BHandHLYP) levels of theory in conjunction with Dunning's cc-pVDZ basis set

Molecule	Cis–trans		Conformation cycle		Ortho–para		Homodesmic reaction	
	L1	L2	L1	L2	L1	L2	L1	L2
1	2.98	2.19	1.73	0.44	1.39	0.94	0.85	0.27
2	3.11	2.38	0.77	0.27	0.12	0.70	0.92	0.15
3	6.66	6.34	4.66	4.06	3.92	3.30	2.76	1.90
4	11.62	9.58	8.26	5.92	9.41	6.06	7.90	4.48
5	14.38	13.09	11.24	9.08	15.43	10.72	13.83	10.64

^a Enthalpies in kcal mol^{−1} (calculation details are given under computational methods).

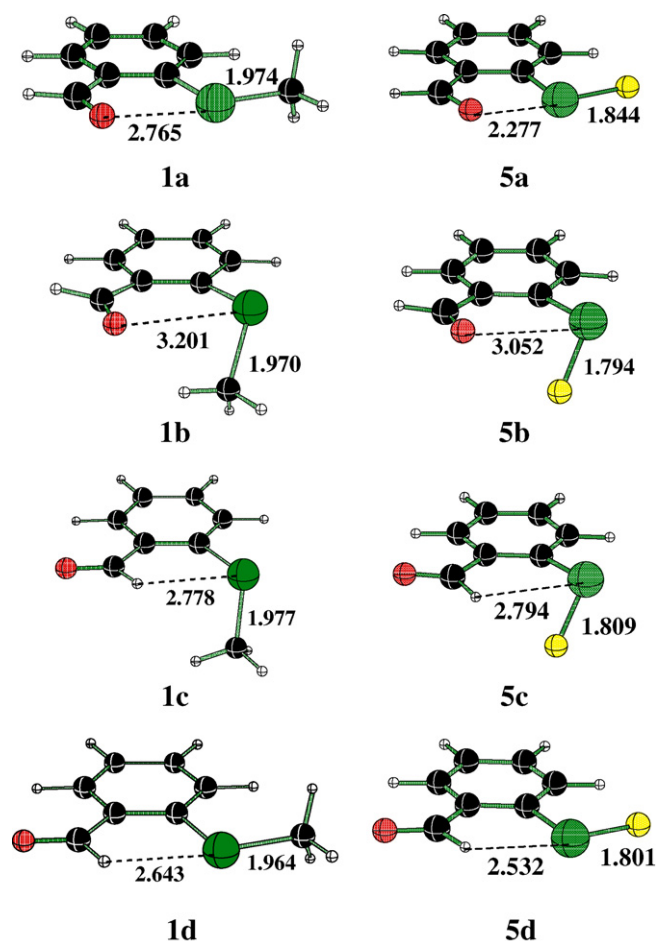


Fig. 2. Se \cdots O and Se-Y distances in different conformers of organoselenium systems **1** and **5** obtained at the B3LYP/cc-pVDZ level of theory.

aryl, the interaction is found to be weaker than when substituted with chloro or fluoro groups, consistent with the increased polarity of Se-Cl/F bond. The general trends in the interaction energy values obtained using different quantification methods are found to be the same. It is noticed that the calculated E_{NB} using the cis-trans and conformation cycle are by and large comparable with those obtained using the homodesmotic reaction scheme as well as the ortho-para method [76,77]. E_{NB} calculated using the cis-trans method is in general higher than those obtained by other three methods.

Another interesting observation pertains to the calculated E_{NB} values using two different density functionals. It has been reported that the computed E_{NB} values with functionals having higher degree of Hartree-Fock exchange tend to agree better with the interaction energies computed using higher-level correlated methods [78]. We have employed Becke-half and half-LYP (BHandHLYP) functional with as high as 50% HF mixing in the present study.

The calculated E_{NB} using a range different method are generally found to be similar. As can be noticed, halogen substituted organochalcogen (**4** and **5**) have significant extent of nonbonded interaction, which could have direct influence on structure and chemical properties of such systems. One of the reasons for such differences in E_{NB} values obtained using the first two methods (as given in Table 1) could arise from another weak stabilizing interaction, namely, the Se \cdots H hydrogen bonding, in conformers **d** and **c** used in the above approaches [79]. As evident from the optimized geometries of **1d** and **5d** (Fig. 2), such additional stabilizing interactions can possibly affect the overall energetics of the cis-trans as well as the thermodynamic cycle approaches. Comparison with earlier estimates indicates a systematic overestimation of E_{NB} values when cis-trans and conformation cycle methods are employed for quantification [80].

Additional calculations using the second-order Møller-Plesset perturbation theory (MP2) has been performed to be able to compare the E_{NB} s obtained using the DFT based methods (Table S4, Supplementary Material). The agreement between the B3LYP and MP2 nonbonding interaction energies is found to be reasonably good with a systematic over estimation with DFT methods with both cis-trans and conformation cycle approaches [81]. More interestingly, the predicted trends at different theoretical levels as well as with the adopted quantification methods for these ranges of substituents are nearly identical when the nature of acceptor group (Se-Y) is changed.

The B3LYP and BHandHLYP optimized geometries of model organoselenium systems are in general in good agreement with those reported previously [29]. Interesting geometrical differences have been noticed between conformers with and without nonbonding interactions. A representative series of optimized geometries for compounds **1**

Table 2

Se \cdots O and Se-Y distances in different conformers of organoselenium systems studied at the BHandHLYP/cc-pVDZ level of theory^a

Molecule/conformer	Se \cdots O distance (in Å)				Se-Y distance (in Å)			
	a	b	c ^b	d ^b	a	b	c	d
1	2.786 (2.765)	3.165 (3.201)	2.764 (2.778)	2.643 (2.643)	1.948 (1.974)	1.949 (1.970)	1.954 (1.977)	1.941 (1.964)
2	2.778 (2.760)	3.134 (3.159)	2.783 (2.797)	2.643 (2.646)	1.928 (1.951)	1.925 (1.943)	1.925 (1.944)	1.919 (1.940)
3	2.634 (2.611)	3.079 (3.110)	2.791 (2.804)	2.611 (2.607)	1.861 (1.879)	1.842 (1.853)	1.846 (1.857)	1.836 (1.849)
4	2.418 (2.335)	3.087 (3.113)	2.775 (2.789)	2.565 (2.519)	2.238 (2.293)	2.192 (2.223)	2.202 (2.235)	2.182 (2.217)
5	2.334 (2.277)	3.034 (3.052)	2.774 (2.794)	2.583 (2.532)	1.808 (1.844)	1.769 (1.794)	1.781 (1.809)	1.771 (1.801)

^a B3LYP/cc-pVDZ optimized distances are given in parenthesis.

^b Refers to the Se \cdots H.

and **5** are provided in Fig. 2. Evidently, the Se \cdots O interaction distances are shortest in conformers **1a** and **5a** and longest in **1b** and **5b**. Inspection of Se \cdots O distances in corresponding conformers of other compounds as given in Table 2 also follows the same trend. Based on the alignments of participating donor–acceptor orbitals this should indeed be so, where the nonbonding interaction is maximized by linear arrangement of oxygen lone pair and $\sigma_{\text{Se-Y}}^*$ orbitals. Elongation of Se–Y bond in conformers **1a** and **5a** as compared to other conformers of the same family supports the involvement of $n_{\text{O}} \rightarrow \sigma_{\text{Se-Y}}^*$ nonbonding interaction. For instance, the Se–F distance in **5a** is more than 1.84 Å while that in other conformers are only around 1.80 Å. When the Se–Y bond is orthogonal, nonbonding interaction arising due to orbital interaction is minimal. In all compounds, a fairly good correlation between computed E_{NB} and Se \cdots O distance is noticed. Shorter contact thus implies stronger Se \cdots O nonbonding interactions. Another likely interaction in these compounds arises from intramolecular Se \cdots H hydrogen bonding as shown in **1d** and **5d**. The Se \cdots H distances for **1** through **5** are found to be generally around 2.6 Å irrespective of the nature of Y group attached to the selenium.

Weinhold's Natural Bond Orbital (NBO) method is widely employed in obtaining improved understanding on orbital interactions [82–84]. The second order perturbation energy [$E(2)$] obtained from NBO analysis signifies the extent of orbital interaction as well as the donor–acceptor charge transfer interactions. These delocalizations result in lowering of occupancy of filled localized Lewis type NBOs and population of empty non-Lewis orbitals. Evidently, higher delocalization represents stronger interaction. Computed second order perturbation energies for **1a** through **5a** are summarized in Table 3 [85]. It can be clearly seen that the $E(2)$ values are in perfect concurrence with the computed E_{NB} s obtained using both cis–trans and thermodynamic cycle methods. Further, the Wiberg bond indices (BI) show a gradual increase upon changing the acceptor group on selenium as in **1–5** [86,87]. Atomic charges computed with the natural population analysis (NPA) [88] also indicate a modest electrostatic contribution towards the

nonbonding interactions (Table 3). It is noticed that strongly interacting systems **4** and **5** show increasingly positive charges on selenium atom. These variations primarily arise due to the larger electronegativity difference between Se and the Y group, which renders more polarity to the Se–Y bond.

In order to gain better insights on the nature of the Se \cdots O interaction we have examined the topological properties of electron density using the *Atoms-in-Molecule* analysis and the results are provided in Table 4 [89]. A (3, –1) bond critical point (bcp) along the Se \cdots O bond path has been identified. A representative molecular plot depicting

Table 4

Summary of topological analysis using the AIM^a method at the B3LYP and BHandHLYP levels of theory in combination with cc-pVDZ basis set

Molecule	B3LYP		BHandHLYP	
	$\rho_{\text{bcp}}(\text{Se}\cdots\text{O})$	$\nabla^2\rho_{\text{bcp}}(\text{Se}\cdots\text{O})$	$\rho_{\text{bcp}}(\text{Se}\cdots\text{O})$	$\nabla^2\rho_{\text{bcp}}(\text{Se}\cdots\text{O})$
1	0.021	–0.016	0.020	–0.016
2	0.022	–0.016	0.020	–0.016
3	0.028	–0.021	0.026	–0.021
4	0.049	–0.033	0.040	–0.029
5	0.055	–0.036	0.046	–0.034

^a Topological properties are in a.u.

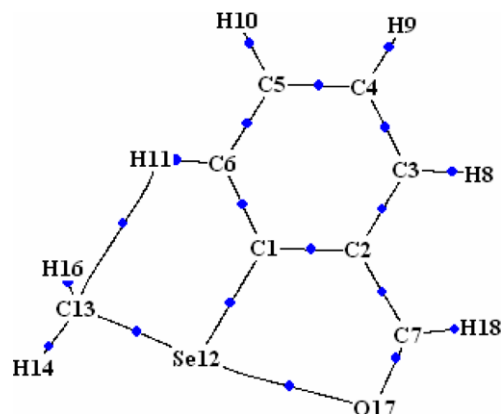


Fig. 3. Molecular plot of **1** (Y = –Me) showing the Se \cdots O bond critical point (Se₁₂ and O₁₇) arising due to intramolecular nonbonding interaction.

Table 3

Summary of NBO analysis at the B3LYP and BHandHLYP levels of theory in combination with cc-pVDZ basis set

Molecule	B3LYP		BHandHLYP					
	$E(2)^a$	BI ^b	Natural charges		$E(2)$	BI	Natural charges	
			O	Se			O	Se
1	6.56	0.06	–0.54	0.46	6.22	0.05	–0.57	0.46
2	6.73	0.06	–0.54	0.47	6.53	0.05	–0.57	0.48
3	11.67	0.09	–0.55	0.53	11.55	0.06	–0.58	0.54
4	37.37	0.24	–0.54	0.57	29.93	0.15	–0.59	0.57
5^c	–	0.28	–0.57	0.84	–	0.20	–0.61	0.86

^a $E(2)$ represents the second order perturbation energy associated with $n_{\text{O}} \rightarrow \sigma_{\text{Se-Y}}^*$ electron delocalization in kcal mol^{–1}.

^b Wiberg bond index for Se \cdots O interaction.

^c When Y = F, the Se–F bond becomes very polar and the NBO analysis recognizes it as a borderline Se⁺ F[–] interaction and fails to identify $n_{\text{X}} \rightarrow \sigma_{\text{Se-F}}^*$ electron delocalization for systems **5**.

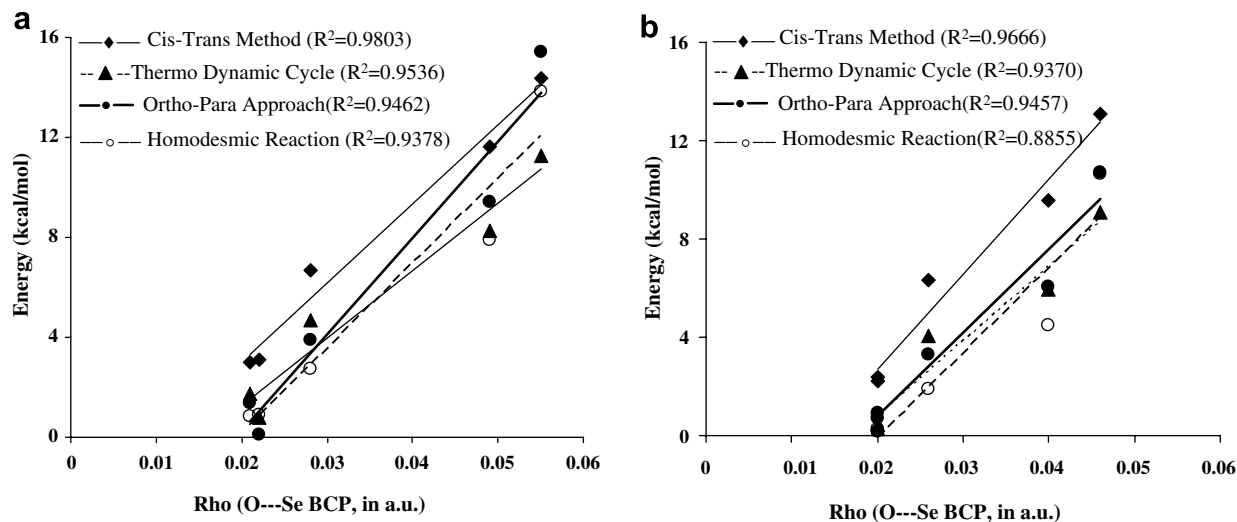


Fig. 4. Correlation plots of nonbonded interaction energies computed using four different methods with $\rho_{bcp}(O \cdots Se)$ at the (a) B3LYP and (b) BHandHLYP levels of theory.

bond-paths and the corresponding bcps for system **1** is given in Fig. 3. A bcp can readily be noticed between interacting chalcogens Se_{12} and O_{17} , which represents the intramolecular nonbonding interactions. Another observation relating to the nature of this interaction emerges from the analysis of topological features of electron density. We have chosen system **1** for this purpose also to highlight the existence of bcp even in the weakest interacting system (E_{NB} s are provided in Table 1) and the Laplacian of electron density ($\nabla^2 \rho_{bcp}$) at the $Se \cdots O$ bond critical point. Calculated $\nabla^2 \rho_{bcp}$ values as given in Table 4 for **1–5** are consistently negative, indicating a predominantly covalent interaction between Se and O atoms [29,37,90,91].

More interestingly in the present context, a good linear correlation between the calculated values for E_{NB} and the electron density (ρ_{bcp}) at the $Se \cdots O$ bond critical points has been obtained. Higher values of ρ_{bcp} are obtained for systems **4** and **5** where the interaction is predicted to be much stronger as compared to other compounds **1–3**. Comparison of these ρ_{bcp} values with more widely known examples such as hydrogen-bonded systems will be worthwhile at this juncture. For instance, the ρ_{bcp} values for hydrogen bonding interaction, $D-H \cdots A$, ranges from 0.002 to 0.035 a.u. [92]. Thus, it can be noticed that the ρ_{bcp} values for **1–3** falls in the range of a standard hydrogen bond, whereas in **4** and **5** is of higher magnitude implying stronger intramolecular interactions [93]. Indeed, the calculated E_{NB} values for **4** and **5** are higher than other systems. The relationship between the E_{NB} values at the B3LYP level (Fig. 4a) is found to be slightly more linear as compared to that obtained using the BHandHLYP functional (Fig. 4b).

We have been able to demonstrate how methods based on a cis-trans conformational approach as well as thermodynamic cycle could be useful in obtaining the strength of intramolecular chalcogen-chalcogen interactions in a series of ortho substituted aryl selenides. These two methods

were also found to be in good agreement with earlier reports using homodesmic and ortho-para approaches.

5. Conclusion

Two methods for quantification of intramolecular interaction energies in a series of ortho substituted arylselenides are proposed. In line with earlier studies, origin of $Se \cdots O$ interaction was identified to be due to orbital interaction involving the delocalization of oxygen lone pair electrons into the suitably aligned $Se-Y$ antibonding orbital ($n_O \rightarrow \sigma_{Se-Y}^*$). Computed interaction energies revealed that the extent of interaction depends strongly on the nature of substituents on selenium. While the quantified interaction energies were found to exhibit similar trends as previous reports based on homodesmic reaction and ortho-para methods, a systematic overestimation was evident in cis-trans and thermodynamic cycle approaches. The computed nonbonding interaction energy values obtained using the DFT methods were in good agreement with that obtained at the MP2(full) method. The quantified interactions were found to correlate well with the structural parameters as well as the topological properties of electron distribution such as the electron density at the $Se \cdots O$ bond critical point obtained using Atoms-in-Molecule analysis.

Acknowledgements

We acknowledge the computer center, IIT Bombay for computing facilities. DR acknowledges CSIR-New Delhi for senior research fellowship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.theochem.2007.01.022](https://doi.org/10.1016/j.theochem.2007.01.022).

References

- [1] R.G.A. Bone, R.F.W. Bader, *J. Phys. Chem.* 100 (1996) 10892.
- [2] W.A. Herrebout, B.J. van der Veken, *J. Am. Chem. Soc.* 119 (1997) 10446.
- [3] J.N.H. Reek, A.H. Priem, H. Engelkamp, A.E. Rowan, J.A.A.W. Elemans, R.J.M. Nolte, *J. Am. Chem. Soc.* 119 (1997) 9956.
- [4] G. Chalasiński, M.M. Szczyński, *Chem. Rev.* 100 (2000) 4227.
- [5] G.J. Gabriel, B.L. Iverson, *J. Am. Chem. Soc.* 124 (2002) 15174.
- [6] C.E. Crespo-Hernández, R. Arce, *J. Phys. Chem. B* 107 (2003) 1062.
- [7] D.H. Nguyen, T.M. Dieckmann, E. Colvin, W.H. Fink, *J. Phys. Chem. B* 108 (2004) 1279.
- [8] J.M. Thomas, N.R. Walker, S.A. Cooke, M.C.L. Gerry, *J. Am. Chem. Soc.* 126 (2004) 1235.
- [9] S.J. Grabowski, W.A. Sokalski, J. Leszczynski, *J. Phys. Chem. A* 108 (2004) 5823.
- [10] X. Wang, K.N. Houk, M. Spichy, T. Wirth, *J. Am. Chem. Soc.* 121 (1999) 8567.
- [11] T. Wirth, *Angew. Chem.* 39 (2000) 3740.
- [12] X. Ren, J. Liu, G. Luo, Y. Zhang, Y. Luo, G. Yan, J. Shen, *Bioconjug. Chem.* 11 (2000) 682.
- [13] G. Mughesh, A. Panda, H.B. Singh, N.S. Puneekar, R.J. Butcher, *J. Am. Chem. Soc.* 123 (2001) 839.
- [14] D.G. Musaev, Y.V. Geletti, C.L. Hill, K. Hirao, *J. Am. Chem. Soc.* 125 (2003) 3877.
- [15] D.G. Musaev, K. Hirao, *J. Phys. Chem. A* 107 (2003) 9984.
- [16] C.W. Nogueira, G. Zeni, J.B.T. Rocha, *Chem. Rev.* 104 (2004) 6255.
- [17] S. Mao, Z. Dong, J. Liu, X. Li, X. Liu, G. Luo, J. Shen, *J. Am. Chem. Soc.* 127 (2005) 11588.
- [18] B.M. Goldstein, S.D. Kennedy, W.J. Hennen, *J. Am. Chem. Soc.* 112 (1990) 8265.
- [19] D.H.R. Barton, M.B. Hall, Z. Lin, S.I. Parekh, J. Reibenspies, *J. Am. Chem. Soc.* 115 (1993) 5056.
- [20] M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.* 118 (1996) 8077.
- [21] H. Komatsu, M. Iwaoka, S. Tomoda, *Chem. Commun.* (1999) 205.
- [22] S. Hayashi, W. Nakanishi, *J. Org. Chem.* 64 (1999) 6688.
- [23] A. Panda, G. Mughesh, H.B. Singh, R.J. Butcher, *Organometallics* 18 (1999) 1986.
- [24] V.I. Minkin, R.M. Minyaev, *Mendeleev Commun.* 10 (2000) 171.
- [25] S. Wu, A. Greer, *J. Org. Chem.* 65 (2000) 4883.
- [26] M. Iwaoka, T. Katsuda, S. Tomoda, J. Harada, K. Ogawa, *Chem. Lett.* 31 (2002) 518.
- [27] M. Iwaoka, S. Takemoto, S. Tomoda, *J. Am. Chem. Soc.* 124 (2002) 10613.
- [28] M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* 124 (2002) 1902.
- [29] M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Am. Chem. Soc.* 126 (2004) 5309.
- [30] M. Iwaoka, H. Komatsu, T. Katsuda, S. Tomoda, *J. Org. Chem.* 70 (2005) 321.
- [31] S.S. Zade, S. Panda, H.B. Singh, R.B. Sunoj, R.J. Butcher, *J. Org. Chem.* 70 (2005) 3693.
- [32] S.K. Tripathi, U. Patel, D. Roy, R.B. Sunoj, H.B. Singh, G. Wolmershauser, R.J. Butcher, *J. Org. Chem.* 70 (2005) 9237.
- [33] L. Zhao, A.G. Cox, J.A. Ruzicka, A.A. Bhat, W. Zhang, E.W. Taylor, *Proc. Natl. Acad. Sci. USA* 97 (2000) 6356.
- [34] G. Mughesh, W.-W. du Mont, *Chem. – Eur. J.* 7 (2001) 1365.
- [35] B.K. Sharma, G. Mughesh, *J. Am. Chem. Soc.* 127 (2005) 11477.
- [36] B.K. Sharma, G. Mughesh, *Inorg. Chem.* 45 (2006) 5307.
- [37] D. Roy, R.B. Sunoj, *J. Phys. Chem. A* 110 (2006) 5942.
- [38] I. Rozas, I. Alkorta, J. Elguero, *J. Phys. Chem. A* 105 (2001) 10462.
- [39] H.G. Kjaergaard, D.L. Howard, D.P. Schofield, T.W. Robinson, S. Ishiuchi, M. Fuji, *J. Phys. Chem. A* 106 (2002) 258.
- [40] S.G. Estacio, P. Cabral do Couto, B.J. Costa Cabral, M.E. Minas da Piedade, J.A. Martinho Simoes, *J. Phys. Chem. A* 108 (2004) 10834.
- [41] P. Lipkowski, A. Koll, A. Karpfen, P. Wolschann, *Chem. Phys. Lett.* 360 (2002) 256.
- [42] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian98, Gaussian Inc.: Pittsburgh PA, 2001.
- [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian03, Gaussian Inc.: Wallingford CT, 2004.
- [44] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [45] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [46] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [47] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [48] A.K. Wilson, D.E. Woon, K.A. Peterson, T.H. Dunning Jr., *J. Chem. Phys.* 110 (1999) 7667.
- [49] H.-G. Korth, M.I. de Heer, P. Mulder, *J. Phys. Chem. A* 106 (2002) 8779.
- [50] M.M. Morlok, K.E. Janak, G. Zhu, D.A. Quarless, G. Parkin, *J. Am. Chem. Soc.* 127 (2005) 14039.
- [51] A.E. Shchavlev, A.N. Pankratov, A.V. Shalabay, *J. Phys. Chem. A* 109 (2005) 4137.
- [52] P. Gilli, V. Bertolasi, L. Pretto, L. Antonov, G. Gilli, *J. Am. Chem. Soc.* 127 (2005) 4943.
- [53] M.-H. Hao, *J. Chem. Theory Comput.* 2 (2006) 863.
- [54] H. Raissi, A. Nowroozi, M. Roozbeh, F. Farzad, *J. Mol. Struct.* 787 (2006) 148.
- [55] A.E. Shchavlev, A.N. Pankratov, A.V. Shalabay, *Int. J. Quantum. Chem.* 106 (2006) 876.
- [56] H.-J. Song, H.-M. Xiao, H.-S. Dong, *J. Phys. Chem. A* 110 (2006) 6178.
- [57] A.S. Özen, F. De Proft, V. Aviyente, P. Geerlings, *J. Phys. Chem. A* 110 (2006) 5860.
- [58] H.-J. Song, H.-M. Xiao, H.-S. Dong, *J. Chem. Phys.* 124 (2006) 074317 (available online: <http://jcp.aip.org/>).
- [59] D. Xie, Y. Zhou, D. Xu, H. Guo, *Org. Lett.* 7 (2005) 2093.
- [60] J.L. Radkiewicz, H. Zipse, S. Clarke, K.N. Houk, *J. Am. Chem. Soc.* 118 (1996) 9148.
- [61] I. Alkorta, I. Rozas, J. Elguero, *J. Org. Chem.* 62 (1997) 4687.
- [62] M.-L. Tsao, C.M. Hadad, M.S. Platz, *J. Am. Chem. Soc.* 125 (2003) 8390.
- [63] B. Wang, J.F. Hinton, P. Pulay, *J. Phys. Chem. A* 107 (2003) 4683.
- [64] E. Ruiz, D.R. Salahub, A. Vela, *J. Phys. Chem.* 100 (1996) 12265.
- [65] J.A. Anderson, G.S. Tschumper, *J. Phys. Chem. A* 110 (2006) 7268.
- [66] Y. Zhao, D.G. Truhlar, *J. Chem. Theory Comput.* 1 (2005) 415.
- [67] T. He, J. Grafenstein, E. Karka, D. Cremer, *Mol. Phys.* 98 (2000) 1639.

- [68] W. Nakanishi, S. Hayashi, A. Sakaue, G. Ono, Y. Kawada, J. Am. Chem. Soc. 120 (1998) 3635.
- [69] W. Nakanishi, S. Hayashi, N. Itoh, J. Org. Chem. 69 (2004) 1676.
- [70] S. Hayashi, H. Wada, T. Ueno, W. Nakanishi, J. Org. Chem. 71 (2006) 5574.
- [71] N. Gresh, J.E. Šponer, N. Špačková, J. Leszczynski, J. Šponer, J. Phys. Chem. B 107 (2003) 8669.
- [72] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
- [73] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO Version 3.1.
- [74] F. Biegler-König, J. Schonbohm, D. Bayles, J. Comp. Chem. 22 (2001) 545.
- [75] F. Biegler-König, J. Schonbohm, J. Comp. Chem. 23 (2002) 1489.
- [76] In the ortho–para method the energy difference between ortho and para isomers of ortho/para-formylarylselenides are taken as a quantitative indicator of nonbonding interaction.
- [77] In a homodesmotic reaction both the number and type of the bond is conserved in both sides of a chemical equation. Homodesmotic reaction for quantifying nonbonding interaction energy in orthoformyl arylselenide can be represented as $E(\text{nonbonding}) = E(\text{PhCHO}) + E(\text{PhSeY}) - E(\text{t}) - E(\text{PhH})$; where each energy term is obtained by separate geometry optimizations, $E(\text{t})$ represents the total electronic energy of the parent orthoformyl arylselenide. A representative homodesmotic reaction used in quantifying the H-bonding interaction in conformer 4d is given in [Figure S1 in the supplementary information](#).
- [78] This comparison is made based on the E_{NB} values obtained at the CCSD(T)/cc-pVDZ values using the homodesmotic and ortho–para methods (Ref. [37]). The percentage of Hartree–Fock exchange in B3LYP and BHandHLYP are, respectively, 20% and 50%.
- [79] Please see [Table S2 in supplementary information](#). The $\Delta H(\text{H-Bond})$ is calculated for conformers **c** and **d** using homodesmotic reaction method.
- [80] Please see [Table S3 in supplementary information](#).
- [81] Calculations were carried out at the MP2(full)/cc-pVDZ level.
- [82] D. Kaneno, S. Tomoda, Org. Lett. 5 (2003) 2947.
- [83] I.V. Alabugin, M. Manoharan, F.A. Weinhold, J. Phys. Chem. A 108 (2004) 4720.
- [84] C.F. Tormena, L.C. Dias, R. Rittner, J. Phys. Chem. A 109 (2005) 6077.
- [85] NBO analysis on all compounds in other possible conformers (**b**, **c** and **d**) is verified. We could not find any significant delocalization contributing to the Se···O nonbonding interaction.
- [86] K.B. Wiberg, Tetrahedron 24 (1968) 1083.
- [87] See [Figure S2 and S3 in supporting information](#).
- [88] A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83 (1985) 735.
- [89] R.F.W. Bader, Atoms in Molecules. A Quantum Theory, Oxford University Press, Oxford, UK, 1990.
- [90] N.B. Okulik, R. Pis Diez, A.H. Jubert, J. Phys. Chem. A 107 (2003) 6225.
- [91] G. Raos, A. Famulari, S.V. Meille, M.C. Gallazzi, G. Allegra, J. Phys. Chem. A 108 (2004) 691.
- [92] P.L.A. Popelier, J. Phys. Chem. A 102 (1998) 1873.
- [93] U. Koch, P.L.A. Popelier, J. Phys. Chem. 99 (1995) 9747.