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# Quantification of Intramolecular Nonbonding Interactions in Organochalcogens

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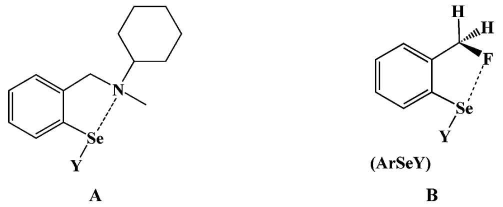
Intramolecular nonbonding interactions between chalcogen atoms in a series of ortho substituted arylselenides (S/O···Se−Y, with Y = −Me, −CN, −Cl, and −F) are quantified using the coupled cluster CCSD(T)/cc-pVDZ level of theory. A homodesmic reaction method as well as an ortho−para approach are employed in evaluating the strength of intramolecular interactions. Comparison of the results obtained using the ab initio MP2 method and pure and hybrid density functional theories are performed with that of the coupled cluster values to assess the quality of different density functionals in evaluating the strength of nonbonding interactions. The interaction energies are found to be higher when the thioformyl group acts as the donor and the Se−F bond acts as the acceptor. In a given series with the same donor atom, the strength of the interaction follows the order Me < CN < Cl < F, exhibiting fairly high sensitivity to the group attached to selenium (Se−Y). Analysis of electron density at the S/O···Se bond critical point within the Atoms in Molecule framework shows a very good correlation with the computed intramolecular interaction energies.

## Introduction

Strong covalent interactions result in stable chemical bonding and lead to well-defined molecular structures, whereas kinetically labile weak noncovalent interactions could render higher reactivity. Over the years, studies on noncovalent interactions have received overwhelming attention owing to their pivotal role in signal transduction, transmembrane ion transport, and a number other physical properties of matter.[1] Noncovalent interactions have been identified to manifest in varied forms such as van der Waals interactions, $\pi$-stacking, cation−$\pi$ interactions, hydrogen bonding, and so on. One of the most popular types of noncovalent interactions is hydrogen bonding, which is much better understood.[2]

One of the important classes of weak nonbonding interactions is known to exist between divalent selenium and other chalcogen atoms. There have been several reports on the importance of intramolecular chalcogen−chalcogen interactions contributing toward the chemical as well as biological activity of organo−selenium compounds.[3] Some popular examples include the role of ebselen and its analogues as a glutathione peroxidase mimetic and the use of selenazafurin as an antiinflammatory drug.[4,7l] A recent study by Mugesh et al. has highlighted the importance of intramolecular coordination in the biological activity of ebselen and other organoselenium compounds.[5] Another interesting application proposed by Wirth et al. is in asymmetric synthesis employing organochalcogens having nonbonding interactions.[6] Some of the very selective examples as stated previously point to the significance of understanding intramolecular chalcogen interactions in greater detail.

Nonbonding interactions in organochalcogens are unequivocally established with the help of structural elucidation primarily based on the distance criteria that the interaction distance should be less than the sum of van der Waals radii of the interacting atoms. While simple distance based criteria continue to thrive as an indicator for the existence of nonbonding interactions, a number of refined methods have also been introduced as better descriptors. Tomoda and others have established the presence of nonbonding interactions in a large number of organochalcogen systems using a combination of techniques such as X-ray crystallography, NMR, and density functional theory calculations.[7] The major factor contributing toward nonbonding interactions in these series of compounds is identified as arising from orbital interactions.



**Y** = SPh $E_{\text{nonbonding}} = 10.8 \pm 1.1$ kcal/mol **Y** = SeAr $E_{\text{nonbonding}} = 0.83$ kcal/mol

**Y** = CN $E_{\text{nonbonding}} = 12.4 \pm 1.6$ kcal/mol **Y** = CN $E_{\text{nonbonding}} = 0.85$ kcal/mol

**Figure 1.** Experimental estimates on the intramolecular nonbonding interactions in arylselenides using NMR chemical shift measurements.

Estimating intermolecular interactions is much less intricate as compared to intramolecular interactions. A large number of experimental and theoretical studies aimed at quantifying intermolecular interactions are found in the literature.[8] Most of these studies revolve around van der Waals complexes as well as hydrogen-bonded systems. In their attempts toward quantifying intramolecular interactions, Tomoda and co-workers have employed NMR techniques to arrive at approximate estimates on intramolecular interactions between Se and N atoms of tertiary amines (Figure 1A) and with F atoms (Figure 1B) in a series of benzylselenides.[7d,7j] To the best of our knowledge, there are no other experimental reports available on the quantification of such an important class of intramolecular interactions.

Theoretical models can offer attractive strategies in quantifying intramolecular interactions. One important protocol toward the quantification of intramolecular interactions is constructing a suitable homodesmic reaction (Scheme 1). In a homodesmic reaction, the number and kinds of bonds on both sides of the

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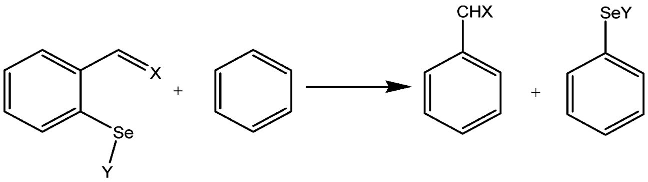
**SCHEME 1: Homodesmic Reaction Approach**



**X = O, S**
**Y = Me, CN, Cl**

equation are conserved, and the associated energy changes reflect the extent of stabilization arising from intramolecular interactions. Impressive results have been obtained by employing isodesmic reactions, a variant of homodesmic reactions, in addressing intramolecular hydrogen bonding.[9] Direct comparison of these systems with experimental data has so far not been possible due to the lack of information on the enthalpy of formation of such intramolecularly bound systems. Another class of systems having intramolecular interactions that are not being studied, both experimentally and theoretically, includes anisaldehydes ($CH_3O-C_6H_4-CHO$). Although the procedure has been in use for estimating the strength of intramolecular hydrogen bonding, there was no systematic attempt to quantify important S/O···Se−Y intramolecular nonbonding interactions.

A quick glance over the last few decades reveals that an increasing number of papers are referring to strong and weak intramolecular chalcogen−chalcogen interactions in many different contexts.[10] Conspicuously absent in the literature are attempts toward systematic quantification of intramolecular interactions. Therefore, in this study, we have decided to investigate an important class of nonbonding interactions with three major objectives: (1) quantifying S/O···Se−Y interactions (where Y = −Me, −CN, −Cl, and −F) using ab initio and DFT methods; (2) evaluating the performance of popular density functionals in studying weak intramolecular nonbonding interactions of the kind stated previously; and (3) studying the relationship between the strength of nonbonding interactions and the topological properties of electron densities. This study is expected to provide a first step toward addressing how strong or weak the intramolecular S/O···Se−Y interactions in organochalcogens are.

## Theoretical Procedures

All calculations were performed with the Gaussian98 and Gaussian03 quantum chemical programs.[11] Full geometry optimizations followed by frequency calculations on the stationary points were carried out at the density functional theories with functionals BLYP, B3LYP, and KMLYP.[12,13] Recently, developed KMLYP functional has been suggested to perform better than the traditional B3LYP functional.[14] The KMLYP functional with a high percentage of Hartree−Fock mixing (55.7%) has been chosen in the present study along with other functionals. Additionally, MP2/6-31G* optimizations were independently carried out using the frozen-core approximation. Single-point energies were evaluated at the second-order Møller−Plesset (MP2)[15] and the coupled cluster theory using single and double excitations with a perturbational treatment of triplet excitations [CCSD(T)] on the MP2/6-31G* geometries. Dunning's correlation consistent basis set of double-$\zeta$ quality, namely, cc-pVDZ, was used for all the calculations.[16] All calculations were done using the bottom-of-the-well energies without the inclusion of zero-point energies. Evaluation of basis set superposition error using the counter-poise correction cannot applied in these systems due to the lack of procedure to separate the super- and subsystems in an intramolecular interaction.

The orbital interaction energies between donor−acceptor orbitals as well as the atomic charges were calculated by using the natural bond orbital (NBO)[17] method at the MP2/cc-pVDZ level using the MP2/6-31G* level optimized geometries. Wiberg bond orders were evaluated at the same level of theory. The Atoms in Molecule analysis was performed by using the AIM2000 program.[18] Topological properties of the electron density ($\rho$) at the bond critical points for the Se···X interactions were evaluated at the MP2, BLYP, B3LYP, and KMLYP levels with the cc-pVDZ basis set on respective optimized geometries, except at the MP2 level, where MP2/6-31G* geometries were used.

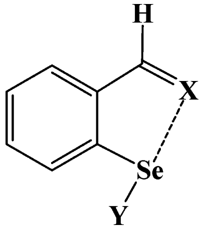
**Methods for Calculating Intramolecular Interactions.** Homodesmic reactions are widely used in predicting molecular stability. The error associated with computing energies of reactants and products is expected to cancel and thus serve as a simple and efficient computational protocol in estimating the energetics.[19] We have designed the homodesmic reaction as shown in Scheme 1, where both the number and the type of bonds are conserved on both sides of the equation and each atom maintains an identical immediate environment. The energy associated with a weak Se···X interaction was calculated as the energy of reaction in Scheme 1. For instance, the nonbonding interaction energy for the Se···O interaction in **3** (where X = O and Y = Cl) can be evaluated using the following equation:

$$E_{\text{(nonbonding)}} = E(\text{PhCHO}) + E(\text{PhSeCl}) - E(\mathbf{3}) - E(\text{PhH})$$

In the second method using the ortho−para approach, the energy difference between isomers, when the nonbonding interaction is turned on (ortho) and turned off (para), is taken as a quantitative measure of the nonbonding interaction. A similar approach has earlier been adopted in addressing intramolecular hydrogen bonding.[20] Evidently, in this method, the electronic interactions operating in the para isomer differ from that in the ortho isomer not only in terms of the absence of intramolecular nonbonding interactions but also in terms of the likely electronic repulsion between chalcogen and donor atom X. Minor differences in delocalization could also be a contributing factor toward the energy difference between ortho and para isomers. Nevertheless, contributions from these effects are expected to be quite small. Moreover, when a series of similar compounds (such as **1**−**4** and **5**−**8**) are compared at uniform levels of theory, the relative differences are more reliable. Thus, the computed intramolecular interactions using the ortho−para method are expected to be good enough to make reliable predictions.

## Results and Discussion

In ortho formyl substituted arylselenides, the preferred conformation has been earlier reported to be the one with formyl oxygen syn to the selenium atom. The anti orientation is in fact 3.21 kcal/mol higher in energy as compared to the syn conformer at the B3LYP/6-31G* level.[21] Intramolecular interactions between oxygen and selenium atoms have been suggested as the key reason behind such conformational preferences. Further, the intramolecular Se···H interaction is known to be much weaker than the Se···O/S type interactions. In the present work, we are focusing on investigating Se···O/S intramolecular interactions in a series of ortho substituted arylselenides as shown below.



| *X* = *O* | | *X* = *S* | |
|---|---|---|---|
| Y = Me | **1** | Y = Me | **5** |
| Y = CN | **2** | Y = CN | **6** |
| Y = Cl | **3** | Y = Cl | **7** |
| Y = F | **4** | Y = F | **8** |

Intramolecular nonbonding Se···O/S interactions are evaluated using two methods as described previously, namely, the homodesmic reaction method and the ortho−para method. The results obtained using the homodesmic reaction for molecules **1**−**8** are summarized in Table 1. Since the experimental determination of intramolecular interactions is extremely difficult and no such reports are available until now on the systems considered in the present study, we have chosen to compare the computed interaction energies with an affordable and accurate theoretical method such as CCSD(T).[22] Inspection of the computed data reveals that the strength of the nonbonding interaction in a given series is noticeably dependent on the nature of the donor atom X. In general, the sulfur atom of the thioformyl is found to be a slightly better donor as compared to the formyl. This can be ascribed to the larger size and better polarizability of sulfur as compared to oxygen.[23] The interaction energies also exhibit fairly good sensitivity to the acceptor group (Y) attached to the selenium atom. For instance, the interaction energies showed a steady increase in the order Me < CN < Cl < F with both formyl and thioformyl donors. Another method that we have adopted was the ortho−para approach. It can be noticed that the computed interaction energies (Table 2) are by and large in very good agreement with that computed using the homodesmic reaction. The concurrence in the nonbonding interaction energies obtained using two different approaches over a range of theoretical methods is an additional indicator toward higher reliability of the computed values. Further, the magnitude of the intramolecular interaction energies for systems **3**, **4**, **7**, and **8** are evidently quite significant. Nonbonding interactions of this order could have subtle consequences in the chemical and biological activities of these arylselenides.

**TABLE 1: Nonbonding Interaction Energies (in −kcal/mol) Calculated Using the Homodesmic Reaction Method at Different Levels of Theory in Conjunction with the cc-pVDZ Basis Set**

| molecule/theory | CCSD(T) | MP2 | BLYP | B3LYP | KMLYP |
|---|---|---|---|---|---|
| 1 | 0.2 | 0.5 | 1.9 | 0.8 | 0.8 |
| 2 | 2.8 | 3.2 | 4.4 | 3.3 | 3.5 |
| 3 | 5.1 | 5.9 | 11.1 | 7.9 | 6.8 |
| 4 | 10.5 | 11.5 | 16.7 | 13.9 | 13.7 |
| 5 | 1.7 | 1.1 | 0.8 | 0.7 | 1.1 |
| 6 | 1.3 | 2.8 | 3.6 | 1.9 | 1.2 |
| 7 | 6.9 | 9.7 | 17.5 | 13.1 | 9.6 |
| 8 | 13.2 | 16.3 | 23.1 | 19.2 | 17.6 |

**TABLE 2: Nonbonding Interaction Energies (in −kcal/mol) Calculated Using the Ortho−Para Method at Different Levels of Theory in Conjunction with the cc-pVDZ Basis Set**

| molecule/theory | CCSD(T) | MP2 | BLYP | B3LYP | KMLYP |
|---|---|---|---|---|---|
| 1 | 0.1 | 0.4 | 0.7 | 0.1 | 0.1 |
| 2 | 2.8 | 2.7 | 4.9 | 4.0 | 5.4 |
| 3 | 6.9 | 7.5 | 12.4 | 9.6 | 8.5 |
| 4 | 11.3 | 12.2 | 18.4 | 15.6 | 15.6 |
| 5 | 2.5 | 1.6 | 1.0 | 2.2 | 2.4 |
| 6 | 1.4 | 2.9 | 4.1 | 2.6 | 2.2 |
| 7 | 7.1 | 9.9 | 18.4 | 14.5 | 11.1 |
| 8 | 13.9 | 16.8 | 24.7 | 20.9 | 19.5 |

**TABLE 3: Key Geometrical Parameters (in Angstroms and Degrees) of Compounds 1−8 Optimized at the BLYP, B3LYP, and KMLYP Levels of Theory in Conjunction with the cc-pVDZ Basis Set**

| | BLYP | | | B3LYP | | | KMLYP | | |
|---|---|---|---|---|---|---|---|---|---|
| | $r_{\mathrm{Se-}}$-X | $r_{\mathrm{Se}}$-Y | $a_{\mathrm{XSeY}}$ | $r_{\mathrm{Se-}}$-X | $r_{\mathrm{Se}}$-Y | $a_{\mathrm{XSeY}}$ | $r_{\mathrm{Se-}}$-X | $r_{\mathrm{Se}}$-Y | $a_{\mathrm{XSeY}}$ |
| 1 | 2.744 | 2.005 | 174.39 | 2.765 | 1.974 | 174.01 | 2.729 | 1.923 | 173.19 |
| 2 | 2.591 | 1.904 | 172.24 | 2.611 | 1.879 | 171.92 | 2.573 | 1.843 | 171.13 |
| 3 | 2.305 | 2.347 | 176.99 | 2.355 | 2.293 | 176.18 | 2.345 | 2.211 | 174.85 |
| 4 | 2.260 | 1.879 | 171.96 | 2.277 | 1.844 | 170.99 | 2.248 | 1.792 | 169.61 |
| 5 | 3.044 | 2.023 | 179.39 | 3.073 | 1.985 | 179.1 | 3.055 | 1.928 | 178.34 |
| 6 | 2.879 | 1.945 | 176.79 | 2.922 | 1.904 | 176.56 | 2.919 | 1.856 | 175.92 |
| 7 | 2.557 | 2.448 | 178.07 | 2.541 | 2.404 | 178.65 | 2.513 | 2.314 | 179.96 |
| 8 | 2.550 | 1.923 | 175.83 | 2.539 | 1.888 | 175.15 | 2.491 | 1.833 | 173.85 |

In the homodesmic as well as ortho−para methods, the interaction energies computed at the second-order Møller−Plesset perturbation theory are found to be slightly higher than those obtained at the CCSD(T) level. One of the interesting observations at this juncture relates to the performance of different density functionals in reproducing the interaction energies. It can be noticed that the interaction energies are overestimated at the density functional as compared to the benchmark CCSD(T) values. The largest deviations are particularly evident when the pure functional, namely, BLYP, is employed. For example, the interaction energy in compound **8** is around 10 kcal/mol higher than that computed at the CCSD(T) level. The larger differences in the case of compounds **7** and **8**, particularly when pure and hybrid density functionals are employed, might be due to the inherent limitations with the DFT methods in representing charge-transfer interactions.[24] Among the density functional methods that we have used, KMLYP is found to have the smallest deviation as compared to the CCSD(T) values.[25]

Key geometrical parameters obtained at various density functional methods using the cc-pVDZ basis set are provided in Table 3. All geometrical features showed uniformly excellent agreement irrespective of the density functional employed for geometry optimization. The X···Se−Y angles in **1**−**8** were found to remain predominantly linear with values in the range of 170−180°. This observation is consistent with the fact that orbital interactions of the kind $n_{\mathrm{X}} \rightarrow \sigma^*_{\mathrm{SeY}}$ are the major contributing factor in nonbonding interactions discussed here. Interestingly, the deviation from the linear arrangement of interacting centers (X, Se, and Y, i.e., $a_{\mathrm{XSeY}}$) was found to depend on the strength of interaction. For instance, compounds **4** and **8**, in which the strongest nonbonding interactions are predicted, exhibited larger deviations from linear arrangements in a given series. This interesting observation is identified as arising due to an additional interaction between the substituent Y and the aryl hydrogen ortho to the Se−Y group. A weak interaction and a bond critical point (vide infra) are predicted between Y and ortho hydrogen.[26] The distance between Se and donor atom O/S showed a steady decrease with an increase in the intramolecular interaction energies. The work by Tomoda and others has unequivocally established that nonbonding interactions of these kinds arise primarily because of orbital interactions between donor and acceptor orbitals.[7a,7d,7j] For obvious reasons, the acceptor Se−Y bond will undergo elongation, as compared to when a suitably oriented donor at the ortho position is absent. The extent of elongations is verified by comparing the optimized Se−Y distances in PhSe−Y at the same levels of theory.[27] We have also compared the DFT geometrical parameters with those obtained at the MP2/6-31G* level. Impressive concurrence is obtained between the MP2 and the DFT methods.[28]

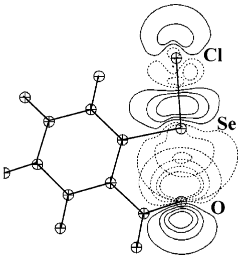


**Figure 2.** Contour diagram of the $n_O \rightarrow \sigma^*_{SeCl}$ interaction.

**TABLE 4: NPA Charges on Se, X, and Y Computed at the MP2/cc-pVDZ//MP2/6-31G* Level of Theory**

| molecule | NPA charges<br>X | <br>Se | <br>Y |
|---|---|---|---|
| 1 | −0.64 | 0.46 | −0.82 |
| 2 | −0.65 | 0.57 | 0.01 |
| 3 | −0.68 | 0.64 | −0.40 |
| 4 | −0.70 | 0.93 | −0.64 |
| 5 | −0.04 | 0.44 | −0.81 |
| 6 | −0.01 | 0.54 | 0.01 |
| 7 | 0.07 | 0.57 | −0.53 |
| 8 | 0.04 | 0.81 | −0.68 |

Weinhold's natural bond orbital (NBO) method has been widely adopted as a tool in analyzing intramolecular nonbonding interactions involving chalcogens.[7c,21] One might intuitively expect that better interactions between donor and acceptor orbitals would facilitate stronger nonbonding interactions. We have identified significant delocalization of lone pair electrons on the donor atom ($n_X$) into the antibonding acceptor orbital ($\sigma^*_{SeY}$). A representative system depicting the stabilizing interaction between the lone pair electrons on the formyl oxygen and the Se−Cl antibonding orbital is given in Figure 2. The natural bond orbital contours of the donor−acceptor pair clearly show that $n_X \rightarrow \sigma^*_{SeY}$ orbital overlap is indeed a contributing factor toward the intramolecular nonbonding interaction.[29] More importantly, in the present context, the extent of delocalization as given by the second-order perturbative stabilization energies exhibited good correlation with the computed nonbonding interaction energies as well as the atomic contact between donor and Se atoms. Greater delocalizations are noticed for the thioformyl series than the corresponding formyl cases.

Natural charges computed at the MP2/cc-pVDZ level in the formyl series, **1**−**4**, indicate negative charges on the donor oxygen and positive charges on the acceptor selenium, indicating an electrostatic stabilization (Table 4). While the charges on selenium remained positive in the thioformyl systems, **5**−**8**, the donor sulfur atoms bear only negligible charges. Thus, the electrostatic contribution toward the nonbonding interaction is prominent when the donor is a more electronegative formyl oxygen than the thioformyl sulfur. Increased polarizability of sulfur should indeed be an additional stabilizing factor, leading to improved intramolecular interactions in the thioformyl series (**5**−**8**).[23]

Inspection of Wiberg bond indices (BI) for the Se···X interaction reveals interesting facts. The correlation between the strength of the nonbonding interaction computed using the homodesmic as well as ortho−para methods and the BI is found to be excellent with a near perfect linear plot.[30] Stronger interactions have higher bond index values and shorter nonbonding contacts. In general, the BIs for systems **5**−**8** are higher as compared to **1**−**4**, consistent with the prediction that thioformyls enjoy greater nonbonding stabilization interactions as compared to the corresponding formyl system.

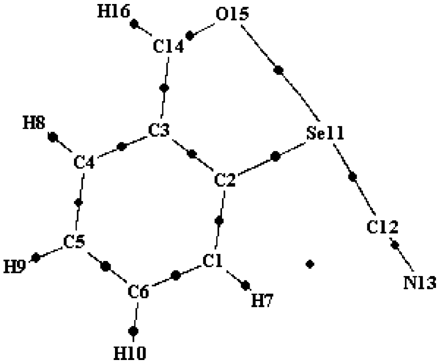


**Figure 3.** Molecular plot of **2** (X = O, Y = −CN) showing the Se···O bond critical point ($Se_{11}$ and $O_{15}$) arising due to intramolecular nonbonding interactions.

**TABLE 5: Summary of the Topological Analysis of the Se···X Bond Critical Points (bcp) Computed at the MP2, BLYP, B3LYP, and KMLYP Levels of Theory in Conjunction with the cc-pVDZ Basis Set[a]**

| | MP2 | | BLYP | | B3LYP | | KMLYP | |
|---|---|---|---|---|---|---|---|---|
| molecule | $\rho_{bcp}$ | $\nabla^2\rho_{bcp}$ | $\rho_{bcp}$ | $\nabla^2\rho_{bcp}$ | $\rho_{bcp}$ | $\nabla^2\rho_{bcp}$ | $\rho_{bcp}$ | $\nabla^2\rho_{bcp}$ |
| 1 | 0.022 | −0.017 | 0.022 | −0.017 | 0.021 | −0.016 | 0.022 | −0.018 |
| 2 | 0.028 | −0.021 | 0.030 | −0.021 | 0.028 | −0.021 | 0.029 | −0.024 |
| 3 | 0.049 | −0.034 | 0.054 | −0.034 | 0.049 | −0.033 | 0.046 | −0.034 |
| 4 | 0.056 | −0.038 | 0.059 | −0.038 | 0.055 | −0.036 | 0.055 | −0.041 |
| 5 | 0.021 | −0.014 | 0.023 | −0.014 | 0.021 | −0.014 | 0.021 | −0.014 |
| 6 | 0.025 | −0.016 | 0.032 | −0.016 | 0.028 | −0.016 | 0.028 | −0.017 |
| 7 | 0.072 | −0.017 | 0.060 | −0.017 | 0.062 | −0.017 | 0.064 | −0.018 |
| 8 | 0.076 | −0.017 | 0.061 | −0.016 | 0.062 | −0.017 | 0.071 | −0.018 |

[a] Topological properties at the Se···X bcp are reported in a.u.

To gain further insight on the nature of nonbonding interactions, we have carried out topological analysis of the electron density with Bader's theory of Atoms in Molecule (AIM).[31] This method has been successfully applied to inspect nonbonding interactions in selenium and tellurium systems apart from their popular applications in the studies involving hydrogen bonding and other weak interactions.[7c,32,33] AIM analysis can be employed in probing the existence of nonbonding interactions as well as in analyzing the strength of such weak interactions.[31a] The presence of a (3,−1) bond critical point along the bond path connecting two interacting atoms is accepted as a standard criterion for the existence of nonbonding interactions. We could identify a (3,−1) bond critical point for a Se···X interaction as depicted in one of the representative cases shown in Figure 3. For all the systems discussed in the present study, the topological properties of electron density such as the density at the bond critical point ($\rho_{bcp}$) and Laplacian of electron density ($\nabla^2\rho_{bcp}$) are analyzed. The summary of AIM analysis on **1**−**8**, performed at different levels of theory using the cc-pVDZ basis set, is presented in Table 5.

The $\rho_{bcp}$ and $\nabla^2\rho_{bcp}$ values obtained at the MP2 and DFT levels are found to be consistently in very good agreement with each other. On the basis of the computed $\nabla^2\rho_{bcp}$ values, which are uniformly negative across all the molecules, it can be said that the nonbonding interactions in **1**−**8** are predominantly covalent in nature. Values of $\rho_{bcp}$ and $\nabla^2\rho_{bcp}$ suggest that the strength of nonbonding interactions in **1**, **2**, **5**, and **6** fall in a similar range as that of standard hydrogen bonding.[34] For all other compounds, the values are typically higher than a hydrogen-bonding situation, indicating a stronger nonbonding interaction. An interesting point central to the present discussion is the relationship between the strength of the computed nonbonding interactions and the values obtained for Se···X $\rho_{bcp}$. The correlation plots between $E_{(nonbonding)}$ versus $\rho_{bcp}$ at respec-

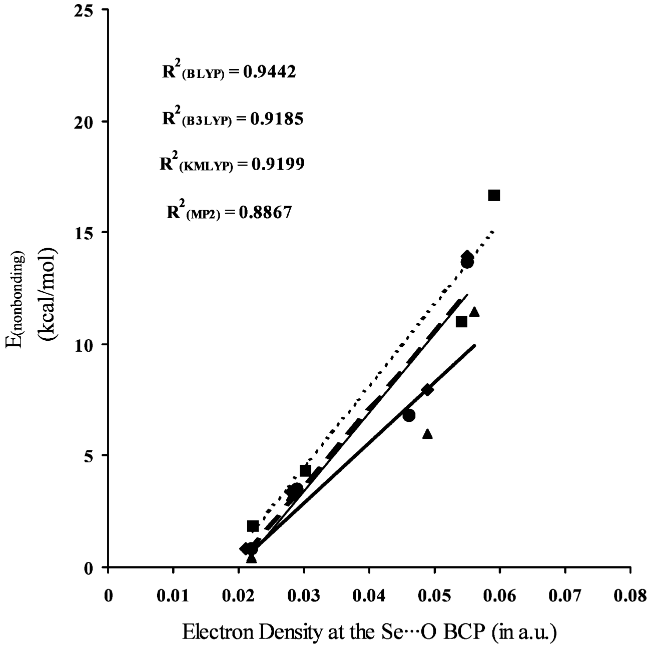


**Figure 4.** Correlation between $E_{nonbonding}$ and $\rho_{bcp}$(Se···O) computed using a homodesmic reaction method for **1**−**4** at the MP2(−▲−), BLYP(--■--), B3LYP(--♦--), and KMLYP(-●-) levels of theory.

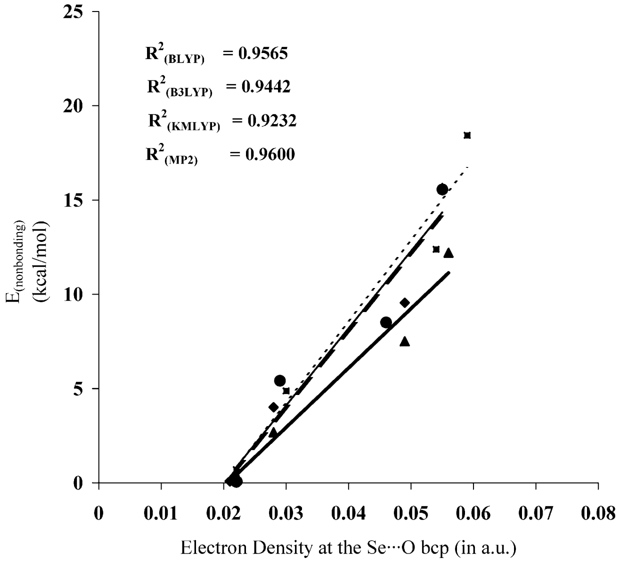


**Figure 5.** Correlation between $E_{nonbonding}$ and $\rho_{bcp}$(Se···O) computed using the ortho−para method for **1**−**4** at the MP2(−▲−), BLYP(--■--), B3LYP(--♦--), and KMLYP(-●-) levels of theory.

tive levels of theory reveal a reasonably good linear relationship between nonbonding interaction energies and the $\rho_{bcp}$ values. The correlation is somewhat better for **1**−**4** (formyl donors) as compared to that for **5**−**8** (thioformyl). Two representative sets are provided in Figures 4 and 5, where $E_{(nonbonding)}$ for systems **1**−**4** obtained using the ortho−para method as well as a homodesmic reaction are correlated with $\rho_{bcp}$.[35]

On the basis of the previous analyses, it can be understood that the topological properties of electron density can be employed as a useful parameter in assessing the strength of Se···O/S intramolecular interactions. We believe that this approach is more refined than the one naively based on the distance criteria. Further, if one can experimentally determine accurate topological features while the structures of such molecules are solved, the strength of the nonbonding interaction can be approximately predicted.

## Conclusions

Quantification of intramolecular interactions in ortho substituted arylselenides revealed that the strength of the interaction depends on both donor atoms and acceptor bonds. The magnitude of the intramolecular interaction energies obtained at the ab initio and density functional theories revealed that the S/O···Se−Y (with Y = −Me, −CN, −Cl, and −F) interaction is strong enough to be of high chemical significance. Among the density functionals examined in the present study, the newly developed hybrid method, KMLYP, was found to be better than the B3LYP and the pure functional BLYP in reproducing the benchmark CCSD(T) interaction energies. On the basis of orbital interactions as well as the Laplacian of the electron density at the bond critical point for Se···X, the interaction was found to be predominantly covalent in nature. A number of other parameters such as the distance and electron density at the bond critical point between S/O···Se showed a good correlation with the computed strength of interaction.

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**Supporting Information Available:** Total electronic energies obtained at different levels of theories, B3LYP/cc-pVDZ and MP2/6-31G* optimized coordinates, geometrical parameters, topological properties of Y···H(Ph) interactions, X···Se bond indices of organochalcogens, correlations between nonbonding interaction energies with S···Se $\rho_{bcp}$, nonbonded interaction energies with the X···Se bond index, and full citations of Gaussian98/Gaussian03. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) See Table S3 in the Supporting Information for further details on the NPA charges and electron densities at the bond critical points.

(27) Geometrical details of PhSe−Y are tabulated in Table S4 in the Supporting Information.

(28) Geometrical details at the MP2/6-31G* level are provided in Table S5 in the Supporting Information.

(29) See Table S6 in the Supporting Information for second-order perturbative stabilization energy values obtained at the NBO/MP2/cc-pVDZ//MP2/6-31G* level.

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(35) See Figures S1 and S2 in the Supporting Information for the correlation of *E*(nonbonding) with S···Se $\rho_{bcp}$ for systems **5**−**8**.