Unusual Attractive Interactions Between Selenium and Oxygen in Selenoiminoquinones

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Abstract: The reaction of benzeneseleninic anhydride and hexamethyldisilazane gives a reactive intermediate namely oligomeric $(RSeN)_4$ which oxidizes a phenol to the selenoiminoquinone **1**. Both spectroscopic and crystallographic studies showed that the oxygen atom of the carbonyl group in the (phenylselenoimino)quinone **2** is involved in an attractive interaction with the selenium atom. The carbon atom of the phenyl ring is also found to be in the same plane as the O–C–C–N–Se plane. Theoretical studies of these systems clearly show a strong dependence of the Se–O interactions on the substituent on the selenium atom. The electronic structure around the selenium atom can be described in terms of the VSEPR model with a 3-center, 4-electron O–Se–R bond and correlated with other hypervalent molecules.

The factors influencing the structures of small and large molecules in terms of electrostatic and dispersive forces are well documented.[1] The effect of intermolecular as well as intramolecular attractive interactions (besides the routinely "discussed" H-bonding interactions) on the conformations of biological macromolecules is a growing field of study.[2,3] Chalcogens are ubiquitous in nature, and the origin and magnitude of these types of interactions involving sulfur or selenium, in particular, have been recently reported in the case of thiazole and selenazole nucleoside analogues by Goldstein and others.[3c] This study further supports the idea of unusual attractive interactions between a chalcogen and an oxygen atom giving rise to additional factors controlling the geometries of small and large molecules. The idea certainly can be extended to systems hitherto unexplored (e.g. participation of the selenium atom of selenamethionine or selenaglutathione peroxidase in these kinds of interactions to further support their secondary or tertiary structures). A good correlation between theoretical and experimental data enhances the predictability of heteroatoms playing key roles in the conformations of molecules. During the course of our mechanistic investigations[4] of the reaction outlined in Scheme I, we observed an interesting behavior in terms of the attractive interaction between selenium and oxygen atoms in (phenylseleno)iminoquinone **2a**. This type of interaction has previously been seen[5,6] for **3** and **4** as shown in Chart I.

In this paper we report the synthesis, crystallographic study, and spectroscopic analysis of (phenylseleno)iminoquinone **2a** along with the (methylseleno)iminoquinone **2b**. In addition, *ab initio* studies of this class of molecules (models) were carried out to further elucidate the nature of this unusual "nonbonded" attractive interaction.

Scheme I

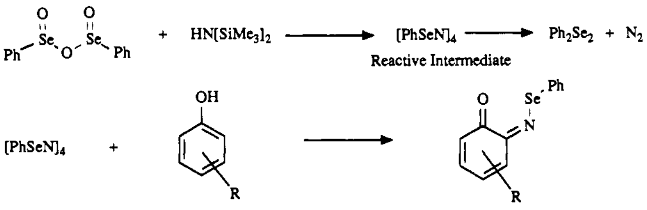

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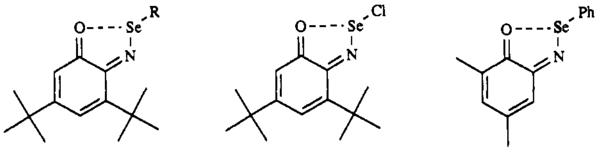
Chart I



2a, R = Ph
2b, R = Me

3

4

Experimental Section

The *ortho* substitution of phenols was accomplished by using benzeneseleninic anhydride and hexamethyldisilazane in chloroform at room temperature to give the corresponding selenoiminoquinones **1** in high yield (Scheme I).[4,7] The (methyl- and (phenylseleno)iminoquinones **2a,b** were prepared (from 3,5-di-*tert*-butylphenol) and characterized using the procedures reported earlier.[4] The ^{77}Se NMR spectra were recorded using a Varian XL 200 spectrometer operating at 39.2 MHz. The data were collected after 932 transients at room temperature, in a 10-mm tube in $CDCl_3$ solvent with a 0.068 M concentration of **2a** and 0.049 M concentration of **2b**.

X-ray Crystallographic Analysis. An orange plate-like crystal of **2a** was mounted on a glass fiber and cooled to 193 K in an N_2 cold stream. The data were collected on a Siemens R3m/V X-ray diffractometer using Mo K_α radiation with a graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares methods. The hydrogen atoms were placed in idealized positions with atomic coordinates riding on adjacent carbon atoms, site occupation factors fixed at 1.0 and isotropic thermal parameters fixed at 0.08 Å^2.[8] Neutral atom

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Table I. Summary of Crystallographic Data[a]

formula	$C_{20}H_{25}NOSe$	temp, K	–139
crystal system	triclinic	diffractometer	Siemens R3m/V
space group	$P\bar{1}$	radiation	Mo Kα
a, Å	5.986(2)	μ, mm^{-1}	1.838
b, Å	9.438(5)	transmission factor range for imperical absorption correction	0.9164–0.5763
c, Å	17.314(7)	2θ limit	$4.0° \leq 2\theta \leq 50.0°$
α, deg	100.84(4)	no. of reflcns measured	3088
β, deg	94.78(3)	no. of unique reflcns, $[I > 2.00\sigma(I)]$	2970
γ, deg	104.05(3)	no. of least-squares parameters	209
Z	2	R[a]	0.043
V, Å^3	923.4(7)	R_w[a]	0.038
density (calcd), g/cm^3	1.346	ρ, e Å^{-3}	$0.50 > \Delta(\rho) > -0.63$
color	orange	Δ/σ max, Δ/σ mean	0.0025, 0.0006
dimensions, mm	$0.06 \times 0.38 \times 0.72$		

[a] $R = \sum|F_o - F_c|/\sum F_o$; $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; $w = 1/(\sigma^2 F + 0.000\,01F^2)$.

scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.[8] Full details about crystal data and refinement are presented in Table I.

Theoretical Details. The *ab initio* calculations used the effective core potentials (ECP) and double-ζ basis sets of Hay and Wadt,[9a] augmented with polarized functions ($\zeta_d = 0.338$) for the Se atom. For all other atoms except H, the ECPs and basis sets with a double-ζ representation of Stevens, Basch, and Krauss[9b] were used. The Dunning–Huzinaga's double-ζ basis set (31) was used for the H atoms.[10] All calculations were performed with the GAMESS package.[11] Since the focus of the present study was to investigate the attractive interactions between Se and O atoms in these selenoiminoquinones, the geometries of the six-membered rings in the models were fixed by employing the data of **2a** in the geometry optimizations. All other structural parameters were optimized using experimental data as the starting geometries.

Results and Discussion

Spectroscopic and Crystallographic Studies. We observed that the carbonyl stretching frequencies in the IR studies of various selenoiminoquinones were much lower than what would be expected of these types of dienones. The carbonyl stretching frequency was 1623 cm^{-1} for **2a** and 1634 cm^{-1} for **2b**; the xylenol derivative **4**[6] shows 1613 cm^{-1}. In addition, the ^{77}Se chemical shifts of the selenoiminoquinones **2a,b** were 1064 and 986 ppm, respectively (referenced to Ph_2Se_2 at 475 ppm), which are unusually downfield for a divalent phenylseleno moiety bonded to a nitrogen atom, which normally occurs in the range 890–925 ppm.[12] These observations clearly lead to a hypothesis of additional weakening of the C=O bond *via* some sort of "nonbonded" interactions of the oxygen atom with participation of the selenium atom as was seen with the xylenol derivative reported by Rogers.[6] Our findings in connection with the observations made by both Sheldrick[5] and Rogers[6] provide better understanding of the magnitude and dependence of these interactions on the ligand effect.

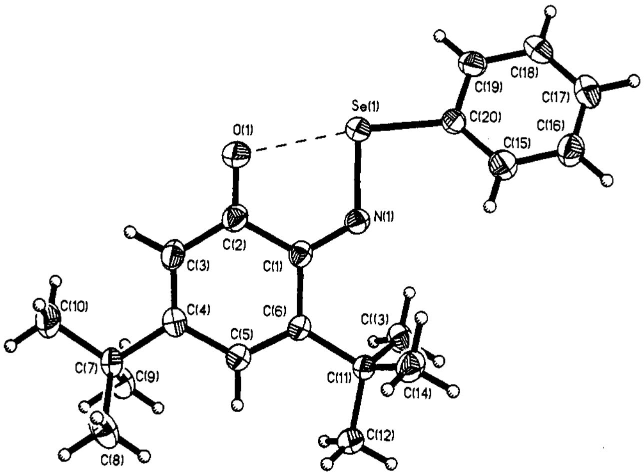

Figure 1. Crystal structure of (phenylseleno)iminoquinone **2a**.

Table II. Bond Lengths (Å) for $C_{20}H_{25}NOSe$[a]

Se(1)–O(1)	2.476(3)	Se(1)–N(1)	1.819(3)
Se(1)–C(20)	1.927(3)	O(1)–C(2)	1.246(5)
N(1)–C(1)	1.302(4)	C(1)–C(2)	1.491(5)
C(1)–C(6)	1.478(5)	C(2)–C(3)	1.440(5)
C(3)–C(4)	1.352(5)	C(4)–C(5)	1.451(5)
C(4)–C(7)	1.531(4)	C(5)–C(6)	1.356(4)
C(6)–C(11)	1.531(4)	C(7)–C(8)	1.542(5)
C(7)–C(9)	1.535(4)	C(7)–C(10)	1.530(5)
C(11)–C(12)	1.540(5)	C(11)–C(13)	1.532(4)
C(11)–C(14)	1.540(4)	C(15)–C(16)	1.381(5)
C(15)–C(20)	1.382(5)	C(16)–C(17)	1.383(5)
C(17)–C(18)	1.386(5)	C(18)–C(19)	1.385(5)
C(19)–C(20)	1.392(5)		

[a] Estimated standard deviations are given in parenthesis.

Table III. Bond Angles (deg) for $C_{20}H_{25}NOSe$[a]

Se(1)–N(1)–C(1)	120.7(2)	Se(1)–C(20)–C(15)	124.8(3)
Se(1)–C(20)–C(19)	114.8(2)	N(1)–Se(1)–C(20)	95.5(1)
N(1)–C(1)–C(2)	120.8(3)	N(1)–C(1)–C(6)	120.4(3)
C(2)–C(1)–C(6)	118.8(3)	O(1)–C(2)–C(1)	117.8(3)
O(1)–C(2)–C(3)	122.6(3)	C(1)–C(2)–C(3)	119.6(3)
C(2)–C(3)–C(4)	119.9(3)	C(3)–C(4)–C(5)	120.2(3)
C(3)–C(4)–C(7)	121.8(3)	C(5)–C(4)–C(7)	117.9(3)
C(4)–C(5)–C(6)	125.2(3)	C(1)–C(6)–C(5)	116.3(3)
C(1)–C(6)–C(11)	121.2(3)	C(5)–C(6)–C(11)	122.4(3)
C(4)–C(7)–C(8)	110.4(2)	C(4)–C(7)–C(9)	107.7(3)
C(8)–C(7)–C(9)	109.0(3)	C(4)–C(7)–C(10)	112.0(3)
C(8)–C(7)–C(10)	109.5(3)	C(9)–C(7)–C(10)	108.3(2)
C(6)–C(11)–C(12)	111.7(3)	C(6)–C(11)–C(13)	110.7(2)
C(12)–C(11)–C(13)	107.1(3)	C(6)–C(11)–C(14)	109.5(2)
C(12)–C(11)–C(14)	107.5(2)	C(13)–C(11)–C(14)	110.3(3)
C(16)–C(15)–C(20)	119.9(3)	C(15)–C(16)–C(17)	120.3(3)
C(16)–C(17)–C(18)	119.9(3)	C(17)–C(18)–C(19)	120.1(3)
C(18)–C(19)–C(20)	119.6(3)	C(15)–C(20)–C(19)	120.2(3)

[a] Estimated standard deviations are given in parenthesis.

The structure of compound **2a** is shown in Figure 1, and the corresponding structural parameters are described in Tables II and III. From Table II, the six-membered ring of the selenoiminoquinone moiety consists of two localized double bonds [C(3)–C(4) = 1.352(5) Å and C(5)–(6) = 1.356(4) Å] and four localized single bonds [C(1)–(2) = 1.491(2) Å, C(2)–C(3) = 1.440(5) Å, C(4)–(5) = 1.451(5) Å, and C(1)–C(6) = 1.478(5) Å] as shown in **2a**. The carbon–oxygen [C(2)–O(1) = 1.246(5) Å] and the nitrogen–oxygen distances [C(1)–N(1) = 1.302(4) Å] are similar

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(8) (a) Diffractometer control program P3VAX. All crystallographic calculations were performed with SHELXTL-PLUS, revision 3.4 (G. M. Sheldrick, Institüt für Anorganishe Chemie der Universitat, Tammannstrasse 4, D-3400 Gottingen, Germany) supplied by Siemens Analytical X-ray Instruments, Madison, WI, on a μVaxII minicomputer. (b) *International Tables for X-Ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

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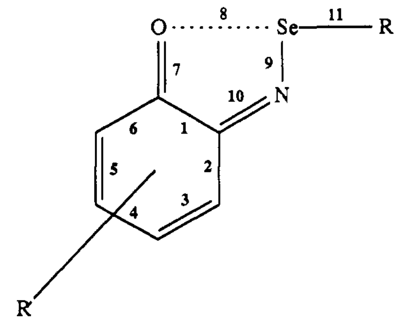
(12) The ^{77}Se chemical shifts are known to have large variations and thereby are highly dependent on the nature of the stereoelectronic environment around the Se atom and on its oxidation state. See: (a) Paulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: New York, 1986. (b) Nicolaou, K. C.; Petasis, N. A. In *Selenium in Natural products Synthesis*; *Cis*, Inc.: Philadelphia, PA, 1984. (c) Liotta, D. In *Organoselenium Chemistry*; John Wiley and Sons: New York, 1987. (d) McFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, *1397*. (e) McFarlane, H. C. E.; McFarlane, W. *Ibid.* 1973, 2416. (f) O'Brien, D. H.; Dereu, N.; Huang, C.-K.; Irgolic, K. J.; Knapp, F. F. *Organometallics* **1983**, *2*, 305. (g) Krief, A.; Hevesi, L. In *Organoselenium Chemistry*; Springer-Verlag: New York, 1988.



1	⇒	1.45 (a), 1.48 (b), 1.49 (c)
2	⇒	1.44 (a), 1.443 (b), 1.48 (c)
3	⇒	1.353 (a), 1.322 (b), 1.356 (c)
4	⇒	1.448 (a), 1.453 (b), 1.451 (c)
5	⇒	1.347 (a), 1.341 (b), 1.352 (c)
6	⇒	1.406 (a), 1.443 (b), 1.441 (c)
7	⇒	1.283 (a), 1.240 (b), 1.246 (c)
8	⇒	2.078 (a), 2.576 (b), 2.476 (c)
9	⇒	1.767 (a), 1.805 (b), 1.820 (c)
10	⇒	1.310 (a), 1.308 (b), 1.302 (c)
11	⇒	- 1.924 (b), 1.927 (c)

Bond Lengths Data

(a) = Sheldrick, *et al.*[5]

(b) = Rodgers, *et al.*[6]

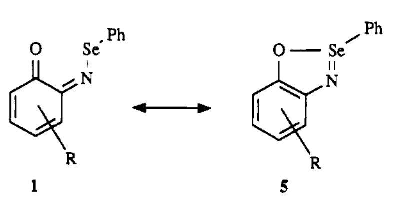
(c) = See Figure 1

Figure 2. Correlation of structural parameters for various selenoiminoquinones.

to those seen for double bonds. The phenylseleno group is joined to the moiety *via* a single bond to the nitrogen atom [Se(1)–N(1) = 1.819(3) Å]. The C(1)–N(1)–Se(1) angle [120.7(2)°] is consistent with the assignment of sp2 hybridization to the nitrogen atom. The atoms Se(1), N(1), C(1) (ring), C(2) (ring), O(1), and C(20) (phenyl) form a plane [$4.133x + 4.591y + 0.909z = 1.829$] with a mean deviation from the plane of 0.02 Å for the six atoms. This implies the possibility of a restricted bond rotation around the Se–N bond, which can only arise from the attractive interaction of Se–O mentioned above. Other intermolecular forces are much less energetic and less directional in nature, and therefore, the restrained structure due to such forces is unlikely.

The Se(1)–O(1) distance [2.4776(3) Å] in **2a** is longer than the sum of their covalent radii (1.89 Å)[13] but shorter than the sum of their Van der Waals radii (ca. 3,4 Å).[14] The selenium–oxygen distance is also longer than that seen for the chloro derivative **3**[5] [2.079(3) Å] but shorter than that seen in the (phenylseleno)-2,4-xylenol derivative[6] **4** [2.575(3) Å] and the trans-ring distances seen in six-membered unsaturated seleno ring systems [2.71–2.89 Å].[15]

As summarized in Figure 2, the carbon–oxygen bond lengths are correlated with the selenium–oxygen distances with the longest length for the chloro derivative **3** [1.283(5) Å] (shortest Se–O distance) and the shortest length for 2-((phenylseleno)imino)-4,6-dimethylcyclohexa-3,5-dienone (**4**) [1.1228(5) Å] (longest Se–O distance). On the other hand, the Se–N bond lengths [1.766(4) (**3**), 1.819(3) (**2**), and 1.805(3) Å (**4**)] do not show any clear correlation with the Se–O distances. These Se–N bond lengths are shorter than the normal Se–N single bonds.[5] These short Se–N bonds have been explained in terms of the involvement of another resonance structure, **5**.[5] The involvement of such resonance contribution would certainly shorten the Se–O and Se–N distances simultaneously. Therefore, this idea can only explain the difference between the phenylseleno derivatives (**2a** and **4**) and the corresponding chloro analogue **3**, but not the same difference between **2a** and **4**.[16]



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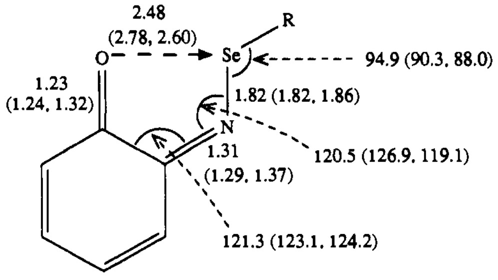
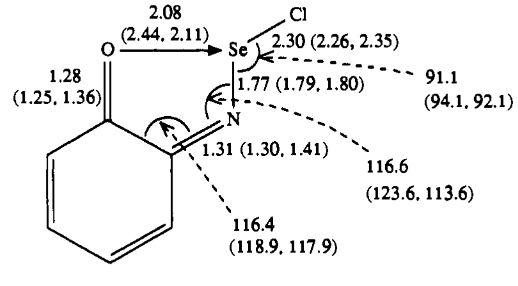


experimental: R = Ph; (theoretical R = H: HF, MP2)



experimental: R = Cl; (theoretical R = Cl: HF, MP2)

Units: Å for bond distance and ° for bond angle

Figure 3. Calculated structural parameters for two model molecules.

The compound **2a** in this paper and **4** reported by Rogers[6] show quite long Se–O (2.48 and 2.58 Å) distances, while the chloro analogue[5] **3** gives a strong Se–O (2.08 Å) interaction. A simple explanation for this significant difference is that the Se–C bond in the phenyl compound exacts a very strong trans influence while the Se–Cl bond does not. However, the detailed bonding around the Se atom in these two compounds should be investigated to explain their differences.

Unfortunately, the methylseleno derivative **2b** was not a crystalline compound and hence we were not able to measure the Se–O distance in this case. Nevertheless, the IR studies showed that the carbonyl stretch is at higher energy than that of the phenylseleno analogue, indicating a stronger C═O bond in the case of the methylseleno derivative. This can be easily interpreted in terms of further weakening of the Se–O interaction.

Theoretical Studies. *Ab initio* geometry optimizations at HF and MP2 levels were performed on the two model compounds as shown in Figure 3. As we can see from Figure 3, the HF results agree very well with the experimental results except for the Se–O distance. However, the significant difference in the Se–O distances between the two molecules was reproduced at the HF level. When the electron correlation is included, the MP2 results predict the Se–O distances quite well, particularly for the chloro analogue. The remaining error (0.12 Å) in the prediction of the Se–O distance in the phenyl compound is probably due to the replacement of the phenyl group by a H atom. Nevertheless, the

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(16) The difference (0.098 Å) in the Se–O bond lengths between **2a** and **4** is substantially significant. However, this observation does not translate into the difference (–0.014 Å) in the corresponding Se–N bond lengths in the same magnitude and trend.

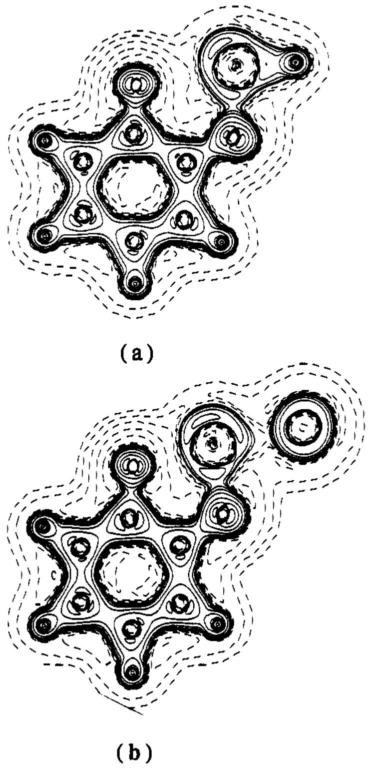
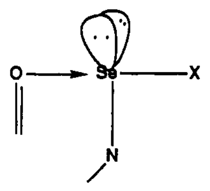


Figure 4. Plots of the Laplacian of the electron density, $-\nabla^2\rho$, on the molecular plane of the two model molecules (see Figure 3 for structures).

calculated Se–O distance is in excellent agreement with the observed Se–O distance reported by Rogers in xylenol derivative **4**. The ring substituents in the xylenol derivative **4** are methyl groups as opposed to *tert*-butyls in **2a**, and they are H atoms in the model compounds chosen for the theoretical studies. The MP2 level overestimated all the other bond distances.

The results of the *ab initio* calculations on a model compound, in which the alkyl and phenyl groups are replaced by H atoms, together with its chloride analogue, where the R group is substituted by a chloride ligand, clearly reproduce this interesting behavior. The nature of the R group seems to modulate the Se–O bond and, thus, the extent of electron density between the selenium and oxygen atoms.

To study the electron charge distribution around the Se atom, we plotted the Laplacian of the electron density, $-\nabla^2\rho$,[17] from *ab initio* HF results in Figure 4. In the contour plot, solid lines denote $-\nabla^2\rho > 0$, where the electron charge is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron charge is locally depleted. As we can see from Figure 4, there are two charge concentrations around the oxygen atom in the molecular plane of both compounds. These concentrations correspond to the oxygen lone pairs. One of the charge concentrations acts as an electron pair to form a dative bond to the Se atom through a hole between the two charge concentrations on selenium. The hole around the Se atom in the chloro derivative is significantly larger than that in the phenyl analogue. On the basis of these electron density analyses, we can qualitatively depict the electronic structure around the Se atom in terms of the VSEPR model[18] shown in **6**. In such a model, we can easily relate the electronic structure of the selenium-containing molecule to its hypervalent analogues. The two lone pairs around the Se atom occupy the equatorial positions of a trigonal-bipyramidal geometry. Because almost all the hypervalent compounds have highly electronegative ligands, the strong Se–O interaction in the chloro analogue is not surprising. The withdrawal of electron density from the Se by Cl is expected to increase the Se–O interaction in a fashion similar to the effect of substituents on the "nonbonded" S–O interactions.[19] The Mulliken population analyses for the models of **2a** and **3** do indeed show significant differences in the charges on selenium and in the overlap populations for the Se–O bonds. In addition, the ^{77}Se NMR chemical shift of **3** (1402 ppm),[20a] being substantially downfield compared to those of **2a** (1064 ppm) and **2b** (986 ppm), further supports the hypothesis of the electron-withdrawing[20b] nature of chloro substitution. In the phenyl derivative, the C (phenyl)–Se bond strongly weakens the corresponding Se–O interaction, and this was confirmed by the crystallographic measurements. Therefore, the highly electronegative Cl ligand in its trans position enhances the 3-center, 4-electron bond and significantly strengthens the Se–O interaction, while the phenyl group, which is covalently bonded to the Se atom, weakens this interaction.



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Conclusion

The crystal structure of **2a** showed the existence of nonbonded Se–O interactions. Comparative studies of various derivatives revealed that the magnitude of such interactions depends on the substituents on the Se atom. With the use of electron density analysis, the electronic structure around the Se atom has been qualitatively described in terms of the VSEPR model and a 3-center, 4-electron bond. This view provides a strong correlation with other hypervalent molecules.

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Supplementary Material Available:

Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all H-atom parameters for **2a** (4 pages); listings of observed and calculated structure factors for **2a** (11 pages). Ordering information is given on any current masthead page.

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