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Molecular and Electronic Structure of Benzeneselenenyl Molecules and Cations

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ABSTRACT

Molecular and electronic structures of a select group of molecules and cations, including benzeneselenenyl chloride, benzeneselenenyl bromide, and benzeneselenol have been studied using ab initio calculations at the Hartree–Fock and MP2 levels of theory. Very few experimental data are available for this class of compounds. The properties and structures of these molecules are compared. © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

We have spent considerable effort in our laboratory examining the use of optical methods of chemical vapor deposition (OCVD) and, in particular, the mechanism of the photodissociation process for the gas phase precursor of the metal atom. Recent work has involved the evaluation of a number of organoselenium molecules [1]. Relatively little structural and spectroscopic information is available for organoselenium molecules or ions in the gas phase [2,3]. As part of the attempt to understand the OCVD experimental differences among these molecules and ions, we have performed a series of ab initio calculations. The molecules of interest, benzeneselenenyl halides and benzeneselenol, have the general molecular formula, C_6H_5SeX (PhSeX, X = H, Cl, or Br, in this instance). In the absence of experimental spectroscopic results, these calculations provide new information concerning the structure of these molecules.

CALCULATIONS

Basis sets for the third row elements are currently under development; however, these complex basis sets have generally been applied to small molecules of only a few atoms. Of the more widely used basis sets, both the STO-3G and 3-21G (and 3-21G*) basis sets are available for Se, as is the LANL1DZ basis set that combines the STO-3G functions for first row atoms and an effective core potential basis set for selenium. Calculations were performed with all of these available basis sets at the Hartree–Fock and MP2 levels of theory, using the GAUSSIAN 92 [4] program. No constraints were imposed on the molecules during geometry optimization. Frequency calculations were performed for all reported geometries to ensure that the structures obtained represented true minima as evidenced by the absence of imaginary vibrational frequencies. Koopmans' theorem [5] was applied to obtain vertical ionization energies for the neutral molecules, and the geometries of the ions were also optimized and used to estimate the adiabatic ionization energies. The nature of the HOMO in these molecules and ions was examined using natural orbitals.

RESULTS AND DISCUSSION

The target molecules have two limiting geometric forms, as indicated subsequently. When selenium is replaced by oxygen, theory and experiment are in agreement that the planar form is preferred for the neutral molecule. The results for sulfur are somewhat ambiguous [6–9], but it appears that, computationally, the neutral sulfur-substituted molecule prefers the perpendicular orientation in apparent contradiction to the experimental data. We have previously reported [10] that neutral benzeneselenol is more stable in the perpendicular form, in agreement with the single available experiment [3]. The pre-

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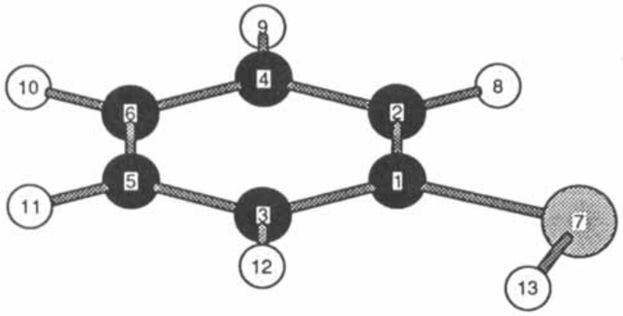
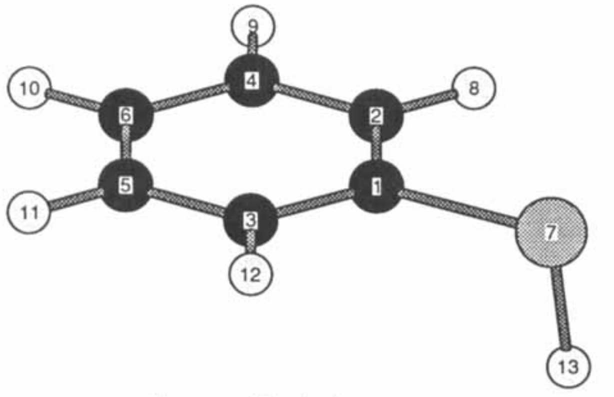
ferred orientations for the cations have not been previously determined either experimentally or computationally. Given the disagreement in the case of sulfur and the absence of any experimental data for the benzeneselenenyl cations, we have chosen to examine the influence of changes in the basis set and level of theory on the geometry of one set of target molecules, PhSeH and PhSeH$^+$. This is an attempt to estimate the effect of basis set complexity on the geometries since the basis sets available for routine use, with a reasonably economic cost for molecules containing selenium, are relatively primitive in comparison with those extensive basis sets available for hydrocarbons.



(planar)



(perpendicular)

The results of the geometry optimizations for PhSeH and PhSeH$^+$, at both HF and MP2 levels of theory and with all available basis sets, are presented in Tables 1 and 2. Examination of the results indicates that the torsional angle of the Se–H is unaffected by the choice of basis set. The absolute values of the bond lengths and bond angles do vary as the complexity of the method changes. The addition of the 6*d* functions to the selenium appears to leave the resulting geometry completely unaffected. The LANL1DZ basis set results in larger C–Se and C–C bond lengths than the split valence basis set and smaller bond lengths for the Se–H bond. The bond lengths increase and the bond C–Se–H angle decreases when electron correlation is included with the 3-21G basis set. Comparison of the PhSeH geometric parameters with the available gas phase electron diffraction (ED) data [3] for PhSeBr indicates that the geometries obtained using the electron correlation method are in poorer agreement than those predicted by the Hartree–Fock method.

Given the number of electrons involved in the halide molecules and cations, the use of the MP2 method is not computationally reasonable and may, in any event, introduce additional error. We have chosen to apply only the HF/3-21G method to the geometry optimizations of the halides and halide cations. These results are shown in Table 3, where the atom labels refer to the geometries shown previously for PhSeH. The computational result may be compared with the experimental, gas phase electron diffraction results for benzeneselenenyl bromide. The calculated C–Se bond length is within 0.01 Å of that from ED, the C–Se–H bond angle is within 0.3° of the experimental value, but the torsional angle is 23° greater (more perpendicular) than the experimental value [3]. The rotational barrier has been calculated to be 4.21 kcal mole^{-1} [10]. The ED measurement may reflect the small barrier for rotation and represent an "average" value of this parameter, since the measurements were performed on a gaseous sample at room temperature. If the ab initio results are used to compute a Boltzmann-weighted average torsional angle, we obtain a value of 76° at 300 K, in excellent agreement with the measurements. A less direct comparison may be made with the solid-state crystallographic data reported for two substantially larger molecules: 2,4,6-tri-*tert*-butylphenyl-iodo-selenium and *o*-formylphenylselenenyl bromide [11,12]. Both of these molecules exhibit the nonplanarity of the phenyl–Se–*X* bond as observed in the current work, and the bond angles and bond lengths are consistent with those reported for the ab initio calculations. The minor differences evident in a structural comparison of the chloride and bromide in Table 3 may be readily attributed to the difference in atomic size between these two halides. Similar effects were observed in the crystallographic experiments [12].

In general and in contrast to phenol, all of the neutral benzeneselenenyl molecules are predicted to exhibit the perpendicular geometry. All of the cations, including phenol, are expected to adopt the planar configuration. The orientation of the neutral molecules may be understood by means of a molecular orbital comparison. At the HF/3-21G level, the HOMO in phenol includes a significant contribution from the oxygen *p* orbital to the π system of the phenyl ring. By contrast, the *p* orbital of the selenium atom does not make such a contribution to the π-electron system. A comparison of the hydrides of the group VI atoms indicates that orbital hybridization becomes less important as one moves down the

TABLE 1 Geometry Parameters for the Neutral Benzeneselenol Molecule

	C–Se	Se–H	C–C	C_1–C_2	C–H	C_2–H_8	$<C_1$–C_2–C_4	$<C_2$–C_1–C_3	$<C_2$–C_4–C_6	$<C_1$–C_2–H_8	$<C_2$–C_4–H_9	$<C_1$–Se–H_{13}
[a]HF/LANL1DZ	1.961	1.470	1.396	1.397	1.072	1.071	119.99	119.92	120.10	120.05	119.71	96.42
[b]HF/3-21G	1.934	1.477	1.383	1.382	1.072	1.070	120.55	119.26	119.93	119.32	119.81	95.83
[c]HF/3-21G(6*d*)	1.935	1.477	1.383	1.382	1.072	1.070	120.55	119.25	119.93	119.32	119.81	95.87
[d]MP2/3-21G(6*d*)	1.951	1.495	1.405	1.404	1.087	1.086	120.80	118.89	119.95	119.00	119.80	94.93

C–C and C–H refer to average bond lengths, not including those specific bonds shown.

[a] The out-of-plane angle for the Se–H group is 88.84.

[b] The out-of-plane angle for the Se–H group is 89.34.

[c] The out-of-plane angle for the Se–H group is 89.14.

[d] The out-of-plane angle for the Se–H group is 88.99.

TABLE 2 Geometry Parameters for the Benzeneselenol Cation[a]

	C–Se	Se–H	C_1–C_2	C_2–C_4	C_5–C_6	C–H[b]	C_2–H_8	$<C_1$–C_2–C_4	$<C_2$–C_1–C_3	$<C_2$–C_4–C_6	$<C_1$–C_2–H_8	$<C_2$–C_4–H_9	$<C_1$–Se–H_{13}
HF/LANL1DZ	1.856	1.466	1.428	1.393	1.392	1.070	1.072	119.32	120.46	120.24	120.68	119.61	98.27
HF/3-21G	1.845	1.472	1.412	1.380	1.402	1.070	1.071	119.78	119.97	120.06	119.82	119.68	96.93
HF/3-21G(6*d*)	1.845	1.473	1.412	1.380	1.402	1.070	1.071	119.80	119.96	120.06	119.84	119.69	96.94
MP2/3-21G(6*d*)	1.868	1.490	1.426	1.353	1.406	1.084	1.086	120.93	118.45	119.18	118.71	120.96	93.80

[a] The cation is planar to within 0.05° for all methods shown.

[b] Average C–H bond length, except for C_2–H_8. The range is less than 0.0005 Å.

TABLE 3 HF/3-21G Geometry Parameters for Benzeneselenenyl Halide Molecules and Cations

	C–Se	Se–X	C_1–C_2	C_1–C_3	C_2–C_4	C_5–C_6	C–H	C_2–H_8	$<C_1$–C_2–C_4	$<C_2$–C_1–C_3	$<C_2$–C_4–C_6	$<C_1$–C_2–H_8	$<C_2$–C_4–H_9	$<C_1$–Se–X_{13}	Bend[a]
PhSeCl	1.910	2.354	1.384	1.384	1.381	1.384	1.071	1.070	120.31	119.67	119.77	119.35	119.92	98.75	89.34
$PhSeCl^+$	1.846	2.355	1.417	1.406	1.379	1.402	1.070	1.072	119.55	120.28	120.06	120.26	119.57	102.25	0.10
PhSeBr	1.914	2.485	1.384	1.384	1.382	1.384	1.071	1.070	120.38	119.54	119.82	119.32	119.89	99.50	88.87
$PhSeBr^+$	1.852	2.509	1.414	1.404	1.381	1.401	1.070	1.072	119.65	120.15	120.07	120.20	119.53	104.32	0.01

[a] Torsional angle, Se–X with respect to phenyl ring.

TABLE 4 Rotational Barriers[a] at the HF/3-21G Level

Molecule	Neutral[b]	cation
PhSeH	−1.34	24.6
PhSeCl	−4.31	22.0
PhSeBr	−4.21	10.8

[a] kcal $mole^{-1}$ (negative values indicate 90°).

[b] Ref. [10].

TABLE 5 HF/3-21G Vertical[a] and Adiabatic Ionization Energies

Molecule	I_v, eV	I_a, eV
PhSeH	9.31	7.30
PhSeCl	9.79	7.91
PhSeBr	9.38	7.64

[a] Via Koopmans' theorem.

group, with the *X*–H bond character increasingly described as an *X p* orbital interacting with the H 1*s* orbital. This same increasing *p*-character interpretation may also apply to the benzeneselenenyl molecules when compared with the sulfur and oxygen analogs.

Rotational barriers for the neutral molecules are small, but the barrier heights increase dramatically for the cations, as shown in Table 4. The cations, all of which are predicted to be planar, may be thought of as containing an sp^2 hybridized Se. Ionization energies, both vertical (by means of Koopmans' theorem) and adiabatic are presented in Table 5. It should be noted that the adiabatic ionization energy for PhSeH increases by 0.4 eV, if electron correlation is included, but the vertical ionization is essentially unchanged.

The Mulliken population analysis is presented in Table 6 for benzeneselenenyl chloride and benzeneselenol as representative of the current calculations,

TABLE 6 Mulliken Charge Distribution (at the HF/3-21G Level)

Atom	*PhOH*	*PhOH*$^+$	*PhSeH*	*PhSeH*$^+$	*PhSeCl*	*PhSeCl*$^+$
C_1	0.379	0.535	−0.488	−0.595	−0.611	
C_2	−0.255	−0.198	−0.179	−0.143	−0.153	−0.157
C_3	−0.288	−0.246	−0.179	−0.156	−0.153	−0.155
C_4	−0.223	−0.219	−0.246	−0.221	−0.250	−0.214
C_5	−0.223	−0.202	−0.246	−0.214	−0.250	−0.214
C_6	−0.260	−0.178	−0.231	−0.132	−0.216	−0.197
H_8	0.263	0.356	0.258	0.350	0.271	0.303
H_9	0.245	0.335	0.246	0.341	0.256	0.314
H_{10}	0.238	0.334	0.246	0.356	0.258	0.316
H_{11}	0.244	0.338	0.246	0.342	0.256	0.315
H_{12}	0.232	0.328	0.258	0.347	0.272	0.328
Se (O)	−0.745	−0.665	0.312	0.508	0.587	1.046
X_{13} (H)	0.392	0.484	0.001	0.083	−0.333	−0.072

along with the computational results for phenol as a comparison. It may be readily observed by comparison of the charges on the oxygen and selenium atoms in Table 6 that the Se atom is much more electropositive than O, so that the direction, as well as the magnitude, of the dipole moment in the selenium-containing molecules is different from that in phenol.

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