

Theoretical studies on the conformations of selenamides

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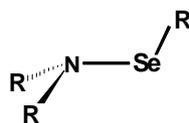
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Abstract. *Ab initio* HF/6-31+G*, MP2/6-31+G*, B3LYP/6-31+G* level calculations have been performed on HSe–NH₂ to estimate the Se–N rotational barriers and N-inversion barriers. Two conformers have been found with *syn* and *anti* arrangement of the NH₂ hydrogens with respect to Se–H bond. The N inversion barriers in selenamide are 1.65, 2.47, 1.93 kcal/mol and the Se–N rotational barriers are 6.58, 6.56 and 6.12 kcal/mol respectively at HF/6-31+G*, MP2/6-31+G* and B3LYP/6-31+G* levels respectively. The $n_N \rightarrow s^*_{\text{Se-H}}$ negative hyperconjugation is found to be responsible for the higher rotational barriers.

Keywords. Selenamides; Se–N interactions; conformations; *ab initio* calculations.

1. Introduction

There is increasing interest in the chemistry of organoselenium compounds. Several selenols, selenones, selenoamides, selenonium ylides, selenonium imides etc. have been studied in comparison with organosulphur compounds¹. Compounds containing Se–N bonds are rare. Flemmang *et al*² have reported the generation of nitrile N-selenides in the gas phase, which have Se–N ionic interactions. They also reported the generation of pyridine N-selenide in the gas phase³. Kamigata *et al*^{4–6} have reported the syntheses, kinetics, optical activity and Se–N interactions of selenonium imides and R₂Se=NR with the Se–N hypervalent bond. In contrast, no theoretical studies have been reported on selenamides (also known as selenenamide and selenohydroxylamine) RSe–NR₂ with Se–N single bond. It is especially intriguing because the corresponding sulphenamides⁷ RS–NR₂ are well-known, their chiroptical properties are well-studied⁸ and sulphenamides are also reported to show a very strong anomeric effect⁹. In our laboratory, we have been studying the bonding characteristics of selenoamides, isoselenocyanates etc. to understand the bonding in organoselenium complexes¹⁰ and also on S–N interactions¹¹.



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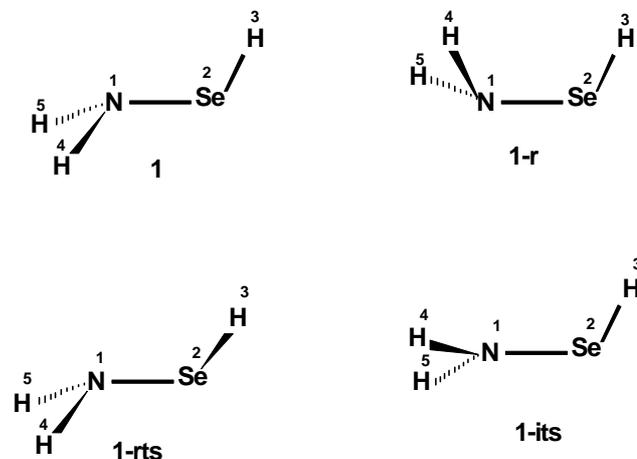


Figure 1. Conformations of selenamides, HSe-NH₂.

In continuation of our efforts, we present studies on the conformational preferences of selenamide, HSe-NH₂ (figure 1), using theoretical methods.

2. Methods of calculation

*Ab initio*¹² and density functional¹³ (DFT) calculations have been carried out using the Gaussian94W¹⁴ package, the Windows version of the Gaussian94 suite of programs, on an IBM compatible PC Pentium-100 MHz with 64 MB memory and 1 GB disk space. Complete optimizations have been performed using HF/6-31+G* basis set. Inclusion of polarization functions in the basis set were found to be important because of the presence of several lone pairs of electrons (in figure 1)^{12a}. To study the effect of electron correlation on the geometries and energies, complete optimizations have been carried out using MP2(full)/6-31+G*, B3LYP/6-31+G*¹⁵ levels also. Frequencies were computed analytically for all optimized species at HF/6-31+G* level in order to characterize each stationary point as a minimum or a transition state and to determine the zero point vibrational energies (ZPE). The frequencies and ZPE values obtained at HF/6-31+G* level have been scaled by a factor of 0.9153¹⁶. Atomic charges in all the structures were obtained using the natural population analysis (NPA) method within the natural bond orbital approach¹⁷⁻¹⁸.

3. Results and discussion

On the potential energy surface of selenamide, HSe-NH₂, two minima, **1**, **1-r**, one rotational transition state, **1-rts**, and one inversion transition state **1-its** could be located (figure 1). Data corresponding to these structures obtained using HF/6-31+G*, MP2(full)/6-31+G*, B3LYP/6-31+G* level are given in table 1. Both the ground state structures **1** and **1-r** are found to have C_s symmetry. The basic difference between the two structures arises from the arrangement of the NH₂ group, *syn* or *anti* with respect to the

Table 1. Geometrical parameters of **1**, **1-r**, **1-its** and **1-its** obtained at HF/6-31+G*, MP2/6-31+G* and B3LYP/6-31+G* levels.

	HF/6-31+G*			MP2/6-31+G*			B3LYP/6-31+G*		
	1	1-r	1-its	1	1-r	1-its	1	1-r	1-its
-Se2	1.833	1.822	1.874	1.867	1.851	1.912	1.873	1.856	1.923
-H4	0.999	0.999	1.003	1.018	1.018	1.023	1.017	1.017	1.022
-H5	0.999	0.999	1.004	1.018	1.018	1.023	1.008	1.017	1.022
-H3	1.464	1.474	1.462	1.482	1.493	1.479	1.494	1.501	1.485
-N1-H5	109.7	110.4	105.8	109.0	110.0	105.0	118.7	109.7	104.5
-N1-H4	111.0	112.8	108.5	109.2	111.5	106.9	120.7	111.7	106.6
-N1-H5	111.0	112.8	106.4	109.2	111.5	104.7	120.7	111.7	104.4
-Se2-H3	96.2	101.0	96.0	95.0	101.3	95.4	99.6	101.5	95.2
-N1-Se2-H3	118.8	63.0	27.0	120.0	61.7	26.3	61.7	120.6	27.6
-N1-Se2-H3	241.2	297.0	140.5	240.0	298.3	137.3	298.3	298.4	137.9
	331.2	336.0	320.7	327.4	333.0	316.6	360.0	333.1	315.5

Se–H bond. The Se–N bond length in **1** is 1.833 Å at HF/6-31+G* level, this distance increases to 1.867 Å and 1.873 Å after including electron correlation at MP2 and B3LYP levels respectively. This is consistent with the earlier observations that inclusion of electron correlation overestimates the S–X bond lengths¹⁹. The calculated Se–N stretching frequencies for **1** and **1-r** at HF/6-31+G* level are 603.37 and 603.7 cm⁻¹ (table 5) with IR intensities 67.35 and 100.86 respectively.

The N–Se–H angle in **1** ~ 95.0° is very small as expected for divalent selenium. The nitrogen is sp³ hybridized and is highly pyramidalized as indicated by the sum of angles (327.4° at MP2/6-31+G* level) around nitrogen in **1**. In **1-r** also, the N atom has pyramidal arrangement but to a lesser degree (sum of angles is 333.0°). At all levels of theory, the Se–N bond length in **1-r** is smaller than that in **1**. The reduction in Se–N bond length from **1** to **1-r** is larger at the electron-correlated levels. In the rotational transition state **1-rts**, the Se–N bond length is elongated by ~0.05 Å. In **1-rts**, the pyramidal character has increased as expected, the sum of angles around nitrogen is 316.6°. The inversion transition state **1-its** has C_s symmetry with a planar arrangement around nitrogen. The Se–N bond in **1-its** is shorter than that in **1** by ~0.06 Å. These variations in the Se–N bond lengths during rotation and inversion can be attributed to the variation in the n_N → s*_{Se–H} negative hyperconjugation.

The absolute energies and the ZPE values of **1** and the related structures are given in table 2, while the relative values are given in table 3. The energy difference (ΔE) between the two minima are only 0.06, 0.24 and 0.03 kcal/mol at HF/6-31+G*, MP2/6-31+G*, and B3LYP/6-31+G* levels respectively. The calculated inversion barriers in **1** are 1.65, 2.47 and 1.93 kcal/mol at these three levels respectively. These smaller ΔE values and inversion barriers indicate that there is no preference for any one of the structures at room temperature. The smaller N-inversion barriers can be attributed to the increased anomeric effect, which stabilizes the transition structure **1-its**. The increase in negative

Table 2. Absolute energies (in a.u.) and zero point vibrational energies (ZPE in kcal/mol) of **1**, **1-r**, **1-rts** and **1-its** obtained at various levels.

Method	1	1-r	1-rts	1-its
HF/6-31+G	-2453.527858	–	-2453.51280	–
HF/6-31+G*	-2453.7611670	-2453.761364	-2453.749850	-2453.757027
MP2/6-31+G*	-2454.042140	-2454.042620	-2454.030846	-2454.036703
B3LYP/6-31+G*	-2455.929739	-2455.929591	-2455.919147	-2455.925150
ZPE [@] (NIF)	23.04 (0)	22.04 (0)	22.52 (1)	22.10 (1)

[@]Obtained at HF/6-31+G* level and scaled by 0.9153; NIF: number of imaginary frequencies

Table 3. The difference (ΔE) between **1** and **1-r**, the rotation and inversion barriers in **1** obtained at various levels. The ZPE corrected values are given in parentheses.

Method	ΔE	Rotation barriers	Inversion barriers
HF/6-31+G	–	9.44 (8.92)	–
HF/6-31+G*	0.12 (0.06)	7.10 (6.58)	2.60 (1.65)
MP2/6-31+G*	0.30 (0.24)	7.09 (6.56)	3.41 (2.47)
B3LYP/6-31+G*	0.09 (0.03)	6.65 (6.12)	2.88 (1.93)

hyperconjugation in **1-its** is evidenced by the decrease in Se–N distance, increase in Se–N bond polarization (table 4) and increase in the N–Se–H and Se–N–H angles in **1-its** as compared to those in **1**.

The Se–N rotational barrier in **1** at HF/6-31+G*(+ZPE) level is 6.58 kcal/mol. Inclusion of electron correlation using second-order Moller–Plesset perturbation method decreases the rotational barrier by a small amount (6.56 kcal/mol). Inclusion of electron correlation using density functional B3LYP method decreases the Se–N rotational barrier to 6.12 kcal/mol. The Se–N rotational barrier in **1** is less than the S–N rotational barrier in sulphenamide, HS–NH₂ (7.97, 8.04, 7.63 kcal/mol at HF/6-31+G*, MP2/6-31+G*, B3LYP/6-31+G* levels respectively). The high rotational barriers in sulphenamides have been attributed mainly to the $n_N \rightarrow s^*_{S-H}$ negative hyperconjugation. The Se–N rotational barrier in **1** is also much larger than is expected for a simple single bond (for example, rotational barrier in C–C single bond is about 3 kcal/mol). Hence, it can be expected that selenamides also show anomeric effects like sulphenamides, albeit to a smaller extent. The reduced Se–N rotation barrier might be due to smaller anomeric effect in **1**, which may arise from the longer bond length (Se–N: 1.833 Å in **1** and S–N: 1.709 Å in HS–NH₂ both at HF/6-31+G* level), which in turn originates from the larger size of selenium.

The *dp–pp* interactions do not seem to play any important role in Se–N interactions. NBO analysis showed that the selenium *d* orbital occupation in **1**, **1-r**, **1-rts** and **1-its** respectively at MP2/6-31+G* level are 0.07, 0.07, 0.07 and 0.06. The inclusion of *d* functions are important so as to polarize the Se–H *s** orbital, but not to cause *dp–pp*

Table 4. NPA charges in **1** and its conformations obtained at MP2/6-31+G* level using MP2 densities.

Atoms	1	1-r	1-rts	1-its
N1	–1.109	–1.114	–1.073	–1.195
Se2	0.206	0.249	0.197	0.287
H3	0.078	0.042	0.072	0.047
H4	0.412	0.412	0.400	0.431
H5	0.412	0.412	0.403	0.431
4d occupancy	0.07	0.07	0.07	0.06

Table 5. Frequencies (cm^{–1}) of different normal modes of vibration in **1** and **1-r** of selenohydroxylamine at HF/6-31+G* level.

Normal modes	1	1-r
Torsion	411.7	446.1
Se–N stretching	603.3	603.7
Scissoring	786.4	771.9
N–Se–H bending	999.1	897.7
Twisting	1081.2	1065.8
Wagging	1645.1	1633.1
Se–H stretching	2361.2	2307.7
N–H stretching symmetric	3447.2	3444.7
N–H stretching asymmetric	3541.5	3543.7

These values are scaled by a factor of 0.9153

interactions⁹. If *dp-pp* interactions are important between selenium and nitrogen, the Se–N rotational barrier should be considerably higher in **1** when the *d*-orbitals are included as compared to the Se–N rotational barrier when they are not included. The Se–N rotational barrier in **1** at HF/6-31+G level is 8.92 kcal/mol which is larger than the Se–N rotational barrier obtained at HF/6-31+G* level (6.58 kcal/mol). Thus, *d*-orbital participation does not increase the rotational barriers, indicating that *dp-pp* interactions are not responsible for the rotational barriers in **1**.

Atomic charges obtained by using the NPA method are given in table 4. The data clearly indicate that the N atom has a unit negative charge whereas the selenium is only slightly positive. In **1-r**, the negative charge on nitrogen slightly increases and the positive charge on selenium increases by 0.043 units, i.e. Se–N bond polarization increases. Variation in the geometrical parameters of **1** and **1-r** indicate relatively more anomeric effect in **1-r** conformation. The change in charge distribution on nitrogen and selenium may be the result of change in hybridization of nitrogen in **1-r** (closer to *sp*²) as indicated by change in the N–Se–H and Se–N–H angles. Because of this increase in the polarization, the electrostatic attraction between selenium and nitrogen increases which finally leads to a decrease in the Se–N distance. This is in accordance with the negative hyperconjugation present in these systems. In the inversion transition state **1-its**, the *s* character and electronegativity of N is more than that in **1**, resulting in increase in the charge at N and reduction in Se–N bond length. This analysis indicates that the smaller Se–N bond distances in selenamides with almost planar arrangement on nitrogen are due more to the increased charge separation between Se and N rather than to the increase in charge transfer from N to Se through *d*-orbital interactions as well as the enhanced anomeric effect.

4. Conclusions

Complete optimizations using SCF, MP2, B3LYP methods and 6-31+G* basis set show that the Se–N in selenamides has a slightly larger Se–N rotational barrier. This is mainly due to the $n_N \rightarrow s^*_{\text{Se-H}}$ negative hyperconjugation present in **1**. The Se–N bond length is of the order of 1.86–1.87 Å. The negative hyperconjugation in **1** is less than that in sulphenamides, mainly due to the larger size of selenium as compared to that of sulphur. The N-inversion barrier is small, which indicates that the two conformers are indistinguishable at room temperature.

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References

1. Whitham G H 1995 *Organosulphur chemistry* (New York: Oxford University Press) p. 85
2. Gerbaux P, Flammang R, Morkved E H, Wong M W and Wentrup C 1998 *Tetrahedron* **39** 533
3. Flemmang R 1999 *Int. J. Mass Spectrosc. Ion Process.* **184** 39
4. Shimizu T, Kamigata N and Ikuta S 1999 *J. Chem. Soc., Perkin Trans. 2* 1469
5. Shimizu T, Seki N, Taka H and Kamigata N 1996 *J. Org. Chem.* **61** 6013
6. Kamigata N, Taka H, Matsuhisa A, Matsuyama H and Shimizu T 1994 *J. Chem. Soc., Perkin Trans. 1* 2257

7. Crain L and Raban M 1989 *Chem. Rev.* **89** 689
8. Blanca M B D, Maimon E and Kost D 1997 *Angew. Chem., Int. Ed. Engl.* **36** 2216
9. Reed A E and Sheleyer P V R 1998 *Inorg. Chem.* **27** 3969
10. Bharatam P V, Uppal P A and Bassi P S 1997 *J. Chem. Phys.* **276** 31
11. (a) Bharatam P V, Uppal P A and Kaur D 2000 *J. Chem. Soc., Perkin Trans. 2* 43; (b) Bharatam P V, Uppal P A and Kaur D 2000 *Indian J. Chem.* **B39** 0000
12. (a) Hehre W J, Radom L, Schleyer P V R and Pople J A 1986 *Ab initio molecular orbital theory* (New York: Wiley-Interscience); (b) Foresman J B and Frisch E 1996 *Exploring chemistry with electronic structure methods* 2nd edn (Pittsburg: Gaussian)
13. (a) Parr R G and Yang W 1989 *Density-functional theory of atoms and molecules* (New York: Oxford); (b) Bartolotti I J and Fluchick K 1996 In *Reviews in computational chemistry* (eds) K B Lipkowitz and D B Boyd (New York: VCH) **17** 187
14. Gaussian 94W 1995 Revision B.2, M J Frisch *et al*, Gaussian, Inc. Pittsburgh PA
15. (a) Becke A D 1993 *J. Chem. Phys.* **98** 5648; (b) Lee C, Yang W and Parr R G 1980 *Phys. Rev.* **B37** 785; (c) Perdew J P and Wang Y 1992 *Phys. Rev.* **B45** 13244
16. Scott A P and Radom L 1996 *J. Phys. Rev.* **B45** 16502
17. Reed A E, Weinstock R B and Weinhold F 1985 *J. Chem. Phys.* **83** 735
18. Reed A E, Curtiss A and Weinhold F 1988 *J. Chem. Phys.* **88** 899
19. Fabian J and Hess B A 1997 *J. Org. Chem.* **62** 1766