Theoretical studies on electron delocalisation in selenourea

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Abstract. *Ab initio* and density functional calculations have been performed on the different possible structures of selenourea (*su*), urea (*u*) and thiourea (*tu*) to understand the extent of delocalisation in selenourea in comparison to urea and thiourea. Selenourea (*su-1*) with C_2 symmetry has the minima on the potential energy surface at MP2(fu)/6-31+G* level. The C–N rotational barrier in selenourea is 8·69 kcal/mol, which is 0·29 and 0·11 kcal/mol more than that of urea and thiourea respectively at MP2(fu)/6-31+G* level. N-inversion barrier is 0·55 kcal/mol at MP2(fu)6-31+G* level. NBO analysis has been carried out to understand the nature of different interactions responsible for the electron delocalisation.

Keywords. Selenourea; electron delocalisation; C–N rotational barriers; N-inversion barriers; NBO analysis; *ab initio* and density functional.

1. Introduction

Biological studies on organoselenium compounds are of current interest[1–9]. Organoselenium compounds like isoselenocyanates (**I**), selenoformamide (**II**) and selenoureas (**III**) are important building blocks for the synthesis of biologically important selenium compounds[2]. For example, selenamides on reaction with 4-tolylnitrile oxide
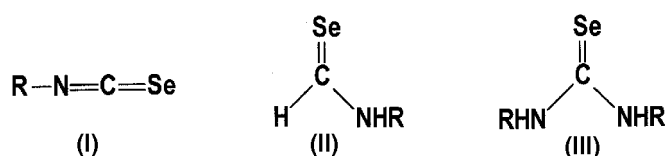

give isoselenocyanates, which on further reaction with amides give selenourea[7]. Selenourea on reaction with *b*ketoesters yields selenouracil[8]. Many cyclic selenoureas have found application in carbohydrate research[9]. Electron delocalisation in these systems plays an important role in their conformational stability and reactivity. For example, molecular flexibility in acylselenoureas has been shown to be controlled by the restricted rotations in the selenourido group[10]. It is important to study the electron delocalisations in selenourea in order to estimate its molecular rigidity.

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Theoretical studies showed that the electron delocalisation in selenoformamide is stronger than that in thioformamide and formamide[11]. Similarly electron delocalisation in selenoisocyanates is stronger than that in thioisocyanates and isocyanates[12]. These facts indicate that the electron delocalisation in selenourea should be larger than that in thiourea and urea. However, since the electronegativity of Se (2·4) is less than that of S (2·5) and O (3·5), according to the resonance model (scheme 1), electron delocalisation in selenourea should be less than that of urea and thiourea. Wiberg *et al*[13a] studied the resonance in amides and thioamides by performing *ab initio* calculations, using density difference maps and concluded that the charge polarization in C–S bond is much weaker and hence the contribution from resonance structure **2** is greatly reduced relative to that in amides (scheme 1). Glendening and Hrabal[14] studied the problem using natural resonance theory and concluded that the weight of the dipolar form increases from formamide to telluroformamide and showed that polarisability of the C–X bond rather than electronegativity of X plays important role in allowing the chalcogen to accommodate more charge density. On the basis of integrated Fermi correlation, Ladig and Camaron[15] showed that the thioamides should be viewed as special cases of amines. Lauvergnat and Hiberty[16] employing valence bond theory showed that resonance stabilization does not wholly account for the C=N bond rotational barriers and the preference of the nitrogen lone pair to stay perpendicular to the molecular plane also should be considered. Wiberg and Rush[14a] as well as Lauvergnat and Hiberty[16] pointed out that the greater charge transfer from N to S in thioamides as compared that from N to O in amides is responsible for the greater electron delocalisation in thioamides. In this paper we report *ab initio* MO and density functional study on the electron delocalisation in selenourea (*su*). Second order electronic interactions in selenourea have been quantitatively estimated using the natural bond orbital method (NBO) and compared with that in urea (*u*) and thiourea (*tu*).

2. Methods of calculation

Ab initio[17] and density functional calculations (DFT)[18] have been performed using the Windows version of the GAUSSIAN94 program[19]. Optimizations have been carried out on different possible structures of urea, thiourea and selenourea including their rotational transition states and inversion transition states etc. at HF/6-31+G* basis set. Since these molecules possess several lone pairs of electrons, diffuse functions have been included in the basis set[17]. To study the effect of electron correlation on the geometry, full optimizations have been carried out at MP2(fu)/6-31+G*[20] and B3LYP/6-31+G*[21] levels. Frequencies have been computed for all optimized structures to characterize each stationary point as a minimum or a transition state and to determine ZPE values. ZPE values have been scaled by the factor of 0·9153[22]. NBO analysis has been carried out to

X = H, NH$_2$
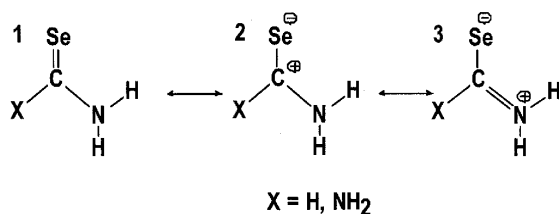
Scheme 1.

understand various second-order interactions. Atomic charges have been estimated using NPA[23] method with MP2 densities at MP2(fu)/6-31+G* level.

3. Results and discussion

3.1 *Geometric structures*

The possible conformations of selenourea are shown in figure 1. *su-2* having C_{2v} symmetry has been found to be the minimum energy structure after complete optimization at HF/6-31+G*. However at electron correlated level MP2/6-31+G* *su-2* showed two negative frequencies which correspond to inversion at two nitrogen atoms. *su-2* having a planar C_{2v} arrangement showed one negative frequency at other theoretical levels like MP2(fu)/6-31+G*, B3LYP/6-31+G* and B3PW91/6-31+G*. *su-1* with C_2 symmetry has been found to be the minimum after complete optimization at MP2(fu)/6-31+G* and B3LYP/6-31+G* levels. The sum of angles around nitrogen 350·1° and 354·5° at MP2(fu)/6-31+G* and B3LYP/6-31+G* levels respectively, indicate the pyramidalization at both nitrogens in *su-1*. These calculations were carried out at other theoretical levels to confirm these results (table 1). It is amply clear that *su-1* with C_2 symmetry is the most preferable structure. *su-3* with C_s symmetry has also been found on
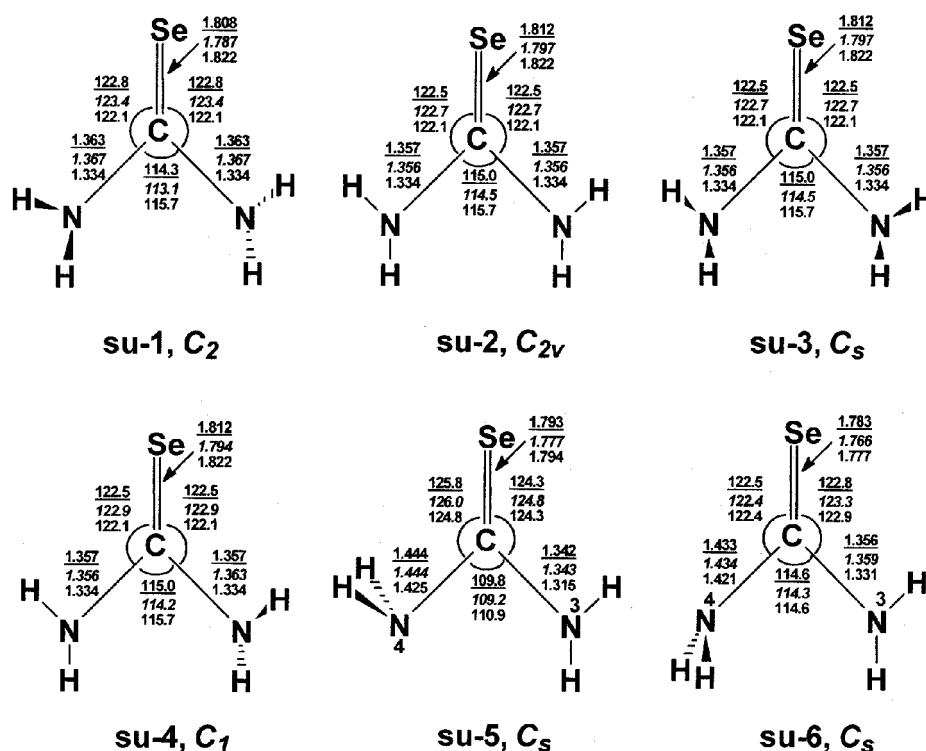

Figure 1. Different structures of selenourea along with their important geometric parameters at three levels, viz. HF/6-31+G*, MP2(fu)/6-31+G* and B3LYP/6-31+G*. Distances are in ångstroms and angles are in degrees.

Table 1. Relative energies (ZPE corrected, in kcal/mol) of various structures of urea, thiourea and selenourea obtained using different theoretical methods.

Structure	Symmetry	HF/6-31+G*	MP2/6-31+G*	MP2(fu)/6-31+G*	B3LYP/6-31+G*	B3PW91/6-31+G*
u-1	C_2	0·00	0·00	0·00	0·00	0·00
u-2	C_{2v}	1·18	2·43	2·31	1·27	1·26
u-3	C_s	1·05	1·35	1·33	0·97	0·99
u-4	C_1	0·90	1·58	1·52	0·87	0·93
u-5	C_s	8·93	8·39	8·40	8·28	8·32
u-6	C_s	15·54	15·11	15·12	14·60	14·73
tu-1	C_2	0·00	0·00	0·00	0·00	0·00
tu-2	C_{2v}	0·02	1·36	1·22	0·45	0·45
tu-3	C_s	–	1·06	1·01	–	–
tu-4	C_1	–	1·02	0·94	0·41	0·42
tu-5	C_s	10·56	8·57	8·58	9·07	9·12
tu-6	C_s	18·85	16·04	16·04	16·57	16·81
su-1	C_2	0·00	0·00	0·00	0·00	0·00
su-2	C_{2v}	0·00	0·73	0·59	0·11	0·11
su-3	C_s	–	0·73	0·60	–	–
su-4	C_1	–	0·64	0·55	–	–
su-5	C_s	11·51	8·68	8·69	9·25	9·28
su-6	C_s	20·43	16·77	16·79	17·11	17·33

the potential energy surface, which has pyramidal arrangement of NH_2 groups towards the same side of the molecular plane. *su-3* showed one negative frequency with almost planar arrangement. *su-1* is only 0·60 kcal/mol lower in energy than *su-3* at MP2(fu)/6-31+G*. The Se–C bond lengths in *su-1* at HF/6-31+G*, MP2(fu)/6-31+G* and B3LYP/6-31+G* are 1·822, 1·787 and 1·808 Å respectively (table 2) which is comparable to experimental bond lengths 1·79–1·84 Å reported using X-ray crystal structure of cyclic selenoureas [10].

The Se–C bond length in *su-1* is slightly longer than the Se–C double bond lengths in $H_2C=Se$ which are 1·722, 1·745 and 1·744 Å at HF/6-31+G*, MP2(fu)/6-31+G* and B3LYP/6-31+G* respectively. This elongation of the Se–C bond in *su-1* in comparison to that in selenoformaldehyde can be attributed to delocalisation of lone pairs on the nitrogens. The C–N bond lengths in *su-1* (1·334, 1·367 and 1·363 Å at HF/6-31+G*, MP2(fu)/6-31+G* and B3LYP/6-31+G* levels respectively) are smaller than the C–N single bond lengths in $H_3C–NH_2$ (1·454, 1·465 and 1·466 Å at HF/6-31+G*, MP2(fu)/6-31+G*, B3LYP/6-31+G* levels respectively) and longer than the double bond lengths in $H_2C=NH$ (1·252, 1·283, 1·273 Å at HF/6-31 + G*, MP2(fu)/6-31 + G*, B3LYP/6-31+G* respectively). This bond shortening in *su-1* clearly supports the delocalisation of the lone pair on nitrogen.

The C–N bond lengths in the three systems are in the order *u-1* (1·388 Å) > *tu-1* (1·374 Å) > *su-1* (1·367 Å) at MP2(fu)6-31+G* level (table 2). Similarly the X–C bond lengths are in the order *u-1* (1·229 Å) < *tu-1* (1·650 Å) < *su-1* (1·787 Å) at the MP2(fu)/6-31+G* level. The pyramidalisation around N is in the order *u-1* > *tu-1* > *su-1* because the sum of angles around nitrogen is in the order *u-1* (343·2°) < *tu-1* > (347·1°) < *su-1* (350·1°). The contraction of the C–N bond lengths and elongation of the X–C bond lengths (relative to the expected X–C bond distance) clearly indicate an increase in the X–C–N electron delocalisation as we move down the group from O to Se.

Table 2. Important geometric parameters of urea (*u-1*), thiourea (*tu-1*) and selenourea (*su-1*) at different levels. Distances are in ångstroms and angles are in degrees

Level	X–C	C–N	X–C–N	j
Urea				
HF/6-31+G*	1·200	1·372	122·8	346·6
MP2/6-31+G*	1·230	1·389	123·2	342·9
MP2(fu)/6-31+G*	1·229	1·388	123·2	343·2
B3LYP/6-31+G*	1·224	1·388	122·9	345·9
B3PW91/6-31+G*	1·222	1·384	122·9	345·8
Thiourea				
HF/6-31+G*	1·680	1·340	122·1	358·0
MP2/6-31+G*	1·652	1·376	123·5	346·7
MP2(fu)/6-31+G*	1·650	1·374	123·5	347·1
B3LYP/6-31+G*	1·673	1·369	122·8	351·2
B3PW91/6-31+G*	1·667	1·365	122·7	351·2
Selenourea				
HF/6-31+G*	1·822	1·334	122·1	360·0
MP2/6-31+G*	1·792	1·369	123·5	349·4
MP2(fu)/6-31+G*	1·787	1·367	124·4	350·1
B3LYP/6-31+G*	1·808	1·363	122·8	354·5
B3PW91/6-31+G*	1·799	1·359	122·8	354·4

3.2 *Rotational and inversion processes*

Two rotational transition states *su-5* and *su-6* with C_s symmetry have been found on the potential energy surface. The difference between them is that *su-5* has *syn* arrangement of Se–C–NH$_2$ unit and *su-6* has *anti* arrangement of Se–C–NH$_2$ unit. Structure *su-6* is higher in energy (8·1 kcal/mol at MP2(fu)6-31+G*) than *su-5* at all levels (table 2) which can be attributed to repulsion between lone pairs on Se and N. The C–N rotational barrier has been calculated to be the difference between *su-1* and *su-5*. The rotational barrier at HF/6-31+G* is 11·51 kcal/mol which is reduced to 8·68 (MP2/6-31+G*), 8·69 (MP2(fu)/6-31+G*) and 9·25 kcal/mol (B3LYP/6-31+G*) after including the electron correlation. This value is much higher than C–N single bond rotational barrier in H$_3$C–NH$_2$, indicating strong restriction in the C–N rotational process. This higher rotational barrier can be attributed to the partial double bond character between C and N. During rotation the C–N bond elongation (0·077 Å at MP2(fu)/6-31+G*) and Se–C bond shortening (0·010 Å at MP2(fu)/6-31+G*) further support the electron delocalisation in selenourea in accordance with resonance model. Table 2 shows that C–N rotational barrier in *su-1* is larger than that *u-1* and *tu-1* at all levels of calculations. The C–N rotational barriers increase in the order *u-1* (8·40) < *tu-1* (8·58) < *su-1* (8·69 kcal/mol) at MP2(fu)/6-31+G* level. The elongation of the C–N bond length and contraction of the X–C bond length during the rotation also follow similar trends, which clearly indicate an increase in the X–C–N electron delocalisation as we move down a group.

Calculations have also been carried out for the N-inversion transition state *su-4* with C_1 symmetry by forcing one of the nitrogens to be planar and allowing the other to optimize. The N-inversion barrier has been calculated to be the difference of *su-1* and *su-4*. The inversion barrier is 0·64 kcal/mol (at MP2/6-31+G*) and 0·55 kcal/mol (at MP2(fu)/6-

31+G*). The N-inversion barrier in *su-1* is lower than *u-1* and *tu-1* at all levels of theoretical calculations. The N-inversion barrier is in the order of *u-1* (1·52 kcal/ mol) > *tu-1* (0·94 kcal/mol) > *su-1* (0·55 kcal/mol) which clearly indicate increasing delocalisation in the order *u-1* < *tu-1* < *su-1*.

3.3 *NBO analysis*

NBO analysis (table 3) shows that $x_N \rightarrow p^*_{C-X}$ delocalisations increase in the order O < S < Se. The second-order energy $E^{(2)}$ associated with this delocalisation in *u-1*, *tu-1* and *su-1* are 56·75, 73·52 and 83·60 kcal/mol respectively at MP2(fu)/6-31+G* level. This trend in delocalisation is further confirmed by the decrease in the electron density of the lone pair on N in the order *u-1* (1·892) > *tu-1* (1·824) > *su-1* (1·807) and increase in electron densities of p^*_{X-C} orbitals in the order *u-1* (0·258) < *tu-1* (0·346) < *su-1* (0·378). The transition state structures *u-5*, *tu-5* and *su-5* are characterized by $n_N \rightarrow s^*_{C-x}$ and $n_N \rightarrow s^*_{C-N}$ negative hyperconjugative interactions which decrease with decrease in the electronegativity of X which is responsible for the increase in the C–N rotational barrier in the order O < S < Se. The atomic charges calculated using the NPA method (table 4) within NBO analysis indicate that C–X bond polarizations decrease in the order, urea (1·742 *e*) > thiourea (0·651 *e*) > selenourea (0·597 *e*) and hence increase in the delocalisations on moving from O to Se.

The above analysis on urea (*u*), thiourea (*tu*) and selenourea (*su*) clearly indicates that the electron delocalisation increase in the order O < S < Se. Since the observed delocalisation order is in apparent contradiction to the resonance model proposed by Pauling because according to the resonance model, electron delocalisation should increase with increase in electronegativity of the element. NBO analysis indicates that orbital interactions rather than electronegativities play an important role in deciding electron delocalisation.

Table 3. NBO analysis of urea (*u*), thiourea (*tu*) and selenourea (*su*) at MP2(fu)/ 6-31+G* level.

Compound	Interaction	Occupancy $r_{n(N)}$	Second-order interaction		
			$E^{(2)\,a}$	$E_{(ej)} - E_{(i)}^{\,b}$	$F_{(i,j)}^{\,b}$
u-1	$n_N - p^*_{O-C2}$	1·892	56·75	0·65	1·177
u-5	$n_{N3} - p^*_{O-C2}$	1·790	94·91	0·58	0·168
	$n_{N4} - s^*_{O-C2}$	1·968	15·14	1·41	0·131
	$n_{N4} - s^*_{C2-C4}$	–	4·35	1·26	0·067
tu-1	$n_N - p^*_{S-C2}$	1·824	73·52	0·52	0·182
tu-5	$n_{N3} - p^*_{S-C2}$	1·720	122·09	0·46	0·213
	$n_{N4} - s^*_{S-C2}$	1·965	11·70	1·06	0·100
	$n_{N4} - s^*_{C2-N3}$	–	6·63	1·25	0·082
su-1	$n_N - p^*_{Se-C2}$	1·807	83·60	0·49	0·189
su-2	$n_N - p^*_{Se-C2}$	1·782	104·52	0·45	0·203
su-5	$n_{N3} - p^*_{Se-C2}$	1·701	132·79	0·44	0·216
	$n_{N4} - s^*_{Se-C2}$	1·963	11·51	0·94	0·093
	$n_{N4} - s^*_{C2-N3}$	–	7·03	1·25	0·084
su-6	$n_{N3} - p^*_{Se-C2}$	1·742	113·28	0·46	0·204
	$n_{N4} - s^*_{Se-C2}$	1·964	2·33	0·92	0·041
	$n_{N4} - s^*_{C2-N4}$		14·10	1·19	0·116

[a] In kcal/mol; [b] in au

Table 4. Atomic charges and group charges in urea, thiourea and selenourea calculated using NBO method.

Structure	X	C	N^3H_2	N^4H_2
u-1	−0·753	0·971	−0·109	−0·109
u-2	−0·777	0·972	−0·098	−0·098
u-3	−0·763	0·969	−0·103	−0·103
u-4	−0·767	0·971	−0·093	−0·111
u-5	−0·739	0·960	−0·054	−0·167
u-6	−0·699	0·959	−0·093	−0·167
tu-1	−0·267	0·384	−0·059	−0·059
tu-2	−0·311	0·398	−0·043	−0·043
tu-3	−0·294	0·392	−0·049	−0·049
tu-4	−0·295	0·393	−0·040	−0·058
tu-5	−0·231	0·356	−0·010	−0·135
tu-6	−0·158	0·342	−0·037	−0·146
su-1	−0·247	0·350	−0·052	−0·052
su-2	−0·284	0·362	−0·039	−0·039
su-3	−0·284	0·362	−0·039	−0·039
su-4	−0·276	0·359	−0·037	−0·047
su-5	−0·198	0·317	−0·017	−0·136
su-6	−0·119	0·300	−0·001	−0·150

Wiberg *et al*[14] have extensively studied the electron delocalisation in formamide and thioformamide. Using density maps and polarisation across C–X bonds they have suggested that the larger C–N barrier in thioformamide relative to formamide can be attributed to larger polarisability of the C–S bond relative to the C–O bond. The valence bond study by Lauvergnant and Hiberty [16] also supported the above arguments. Hence, it may be concluded that the smaller charge separation in the C–Se bond i.e. stronger polarisability of the C–Se bond relative to C–S and C–O bonds is responsible for the stronger electron delocalisation in *su-1*.

4. Conclusions

Ab initio and density functional calculations clearly indicate that electron delocalisation in *su-1* is due to $n_N \rightarrow p^*_{C-X}$ delocalisation as expected from the resonance model. The electron delocalisation in *su-1* is larger than that in urea and thiourea. The increase in the C–N rotational barrier, increase in the Se–X bond length, decrease in the C–N bond length and decrease in the N-inversion barrier can be attributed to the increase in the electron delocalisation in the order of *u-1* < *tu-1* < *su-1*, which is also evidenced by the order of the second-order energy $E^{(2)}$ associated with $n_N \rightarrow p^*_{C-X}$ delocalisation (*u-1* (56·75) < *tu-1* (73·52) < *su-1* (83·60 kcal/mol) at MP2(fu)/6-31+G* level). The stronger electron delocalisation in *su-1* may be attributed to larger polarisability of the Se=C bond.

Acknowledgements

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