121. Stereoelectronic Properties, Stereospecificity and Stabilization of α-Seleno Carbanions. An ab initio Study[1]

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Summary

An *ab initio* study of α-seleno carbanions show that they are subject to appreciable polarization and stereoelectronic effects. Like in α-thia carbanions, the equatorial **e** forms are more stable than the axial **a** forms, one of the stabilizing contributions being the conformation dependent (C^- lone pair, σ* Se–Z) interaction. The carbanion stabilizing effect of the α–Se atom is about 3 kcal/mol larger than that of the sulfur analog. As in the case of the sulfur no specific effect of the d orbitals is found.

Introduction. – Carbanions C–X–Z formed in α position to an heteroatom X (X = O, S; Z = H, CH_3) have been studied experimentally and theoretically (see [1] [2], and references cited therein). The most striking results were (i) the increased acidity of C–H bonds geminal to second row atoms, in particular sulfur, compared to first row atoms, and (ii) the strong stereoelectronic orientational effects present in these carbanions. These results have been related to the greater polarisability of second row atom [1] [2] and to stereoelectronic effects arising from conformational dependent interactions of hyperconjugative type between the C^- lone pair (1p) and an antiperiplanar (app) 1p on the heteroatom X, or between the C^-–1p and the app polar X–Z bond [2]. It has also been shown that $(d\text{–}p)_\pi$ bonding does not contribute to the stabilization of a carbanion (or to the acidity of a C–H bond) by an α-sulfur atom [1] [2].

Our interest in α-seleno carbanions comes both from the recent use of these species as synthetic intermediates in organic chemistry [3–6] and from the extension of our previous theoretical work on α-oxa and α-thia carbanions to the heteroatoms X of the next period. Indeed the heteroatoms of the third period may bring about major effects as compared to those of the second period; for instance, whereas the nitrogen site is planar in $(SiH_3)_3N$, it is pyramidal in both $(CH_3)_3N$ and in $(GeH_3)_3N$

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[1] Stereoelectronic Effects, Part 6; Part 5, see [2].

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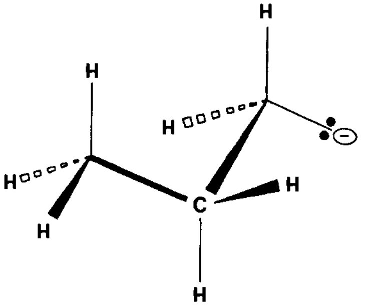
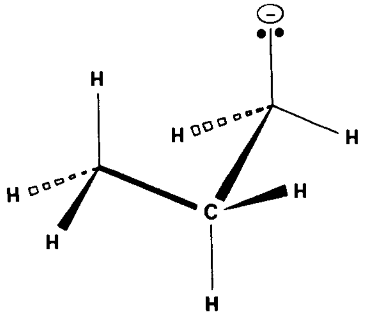
[7]. In the present work we shall compare the effects of Se and S especially with respect to the following questions: does Se stabilize an α-carbanion better than S? are the stereoelectronic orientational effects stronger with Se than with S? do the d orbitals of Se play any significant role?

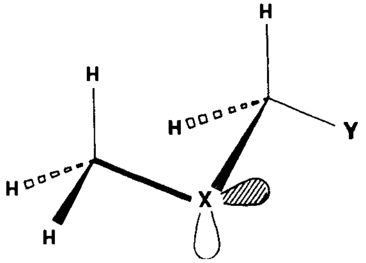
We have performed *ab initio* SCF–LCAO–MO conformations on the following molecules: $^-CH_2$–X–CH_3 (X = CH_2, S, Se) (**1**–**3**), $^-CH_2$–Se–H and the corresponding protonated species³).



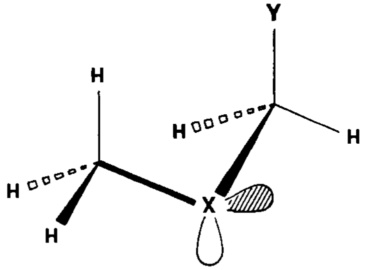
1e



1a



2H X=S Y=H
2e X=S Y= –
3H X=Se Y=H
3e X=Se Y= –



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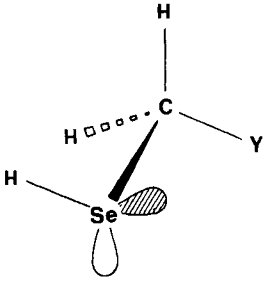
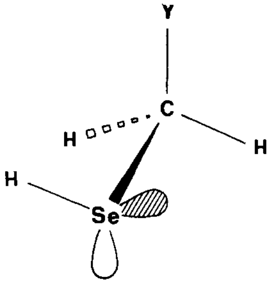
3a X=Se Y= –



4H Y=H
4e Y= –



4a Y= –

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³) We had previously studied the sulfur compounds *2* (see [2]) but with a smaller basis set. In order to make comparisons possible, the new calculations reported here use the same basis set on carbon and hydrogen as in the other species.

Two types of conformations have been studied for each anionic species, the 'equatorial' type **1e**–**4e**, and the 'axial' type (**1a**–**4a**) corresponding, respectively to equatorial and axial orientation of C^-–1p if the fragments **1**–**4** were included in a cyclohexane ring in the conformations shown.

Method of calculation. – The calculations have been performed with the program ASTERIX [8]. In order to save computation time, we have used the same geometry for the two types of anions as for the corresponding acid. Although this restriction may affect quantitatively the computational results, it is very unlikely that it would modify the main conclusions. The following bond lengths have been used: C–C, 1.52 Å; S–C, 1.819 Å, Se–C, 1.98 Å, Se–H, 1.46 Å, C–H, 1.091 Å in **1**, 1.10 Å in the other species. The angles have been taken as tetrahedral, including the carbanionic center⁴), except for ∢ C–S–C = 97.3°, ∢ C–Se–C = 95°, ∢ C–Se–H = 95°.

A Gaussian basis set of single zeta type for the inner shells, and of double zeta type for the valence shells have been used: namely a [8, 4/4] set contracted into [3, 2/2] [10] for the C and H atoms, and a [10,6,1] set contracted into [4,3,1] [11] for the S atom (exponent of the d function: 0.6). For the Se atom, we have optimized a [12,8,5] basis set, contracted into [5,4,2] as follows: a [12,8,4] set has been first optimized on the Se atom in the ^3P state (total energy $E_T = -2399.2066$ a.u.) and contracted in 5s, 4p, 1d, ($E_T = -2394.7269$ a.u.). This set has been enlarged by adding a 5th d function whose exponent, as well as the 8th p function exponent have been optimized on the SeH_2 molecule ($E_T = -2395.9455$ a.u.); the final exponents and the contraction coefficients are reported in *Table 1*.

The geometry optimisation of SeH_2, performed with this basis leads to Se–H = 1.454 Å, ∢ H–Se–H = 93.8°, in satisfactory agreement with the experimental values (respectively 1.47 Å and 91° [12]). The ionization potentials computed on SeH_2, $HSeCH_3$ and H_3CSeCH_3 (*Koopman*'s approximation) reported in *Table 2* agree also with the experimental values. We thus believe that this Se basis set is suitable for our study.

Results. – We have reported in *Table 3* the main energetic results and in *Table 4* some results from the *Mulliken* population analysis⁵). We shall mainly discuss the total protonation energies in terms of polarization effects and stereoelectronic effects, and analyse the role of the d orbitals in **3** and **4**.

1. *Protonation energies. Polarization effects.* In the series $H_3C{-}X{-}CH_2^-$ (**1**, **2** and **3**) and for a given conformation, the proton affinity raises in the order X = Se < S < CH_2. Taking the propyl anion as reference, one sees that the S and Se atoms *α* to a C^--carbanion have a stabilizing effect of respectively 26–20 and 30–23 kcal/mol. In the gas phase, Se should add a stabilization of 3–4 kcal/mol with respect to sulfur; in other words, a C–H bond should be more acidic *α* to Se than *α* to S by around 3p*K* units. This effect of neighbouring X on carbanion stabilization cannot be accounted for by electronegativity arguments (since Se and S have nearly the same electronegativity [13]), but rather by polarization effects; the Se atom being larger

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[4]) CH_3^- is computed to have an inversion barrier of 13.8 kcal/mole and an H–C–H angle of 101° [9]. We have computed for $H_3C{-}S{-}CH_2^-$ an inversion barrier of 11.3 kcal/mole [2], comparable to the inversion barrier of 11.0 kcal/mole found in $H{-}S{-}CH_2^-$ [1a].

[5]) Information available on any other aspect of this work can be obtained on request.

Table 1. *Selenium basis set of Gaussian functions* (12s, 8p, 5d) *contracted into* [5s, 4p, 2d]; *exponents* (α_i) *and contraction coefficients* (C_i)

s Functions		p Functions		d Functions	
α_i	C_i	α_i	C_i	α_i	C_i
110166.	0.00166	787.2	0.02310	49.208	0.07258
16454.	0.01280	186.702	0.15197	13.7737	0.31279
3772.5	0.06176	59.3369	0.44110	4.45	0.52895
1096.0	0.20702	21.3502	0.48726	1.4	0.36502
369.448	0.42560				
135.783	0.39446	6.61516	0.45975	0.33	1.0
		2.31882	0.65091		
34.47	0.40930				
15.1604	0.67456	0.386413	1.0		
4.40667	0.48930				
1.92114	0.75122	0.12	1.0		
0.38505	1.0				
0.15	1.0				

Table 2. *The computed first two Ionization Potentials of* SeH_2, **3H** *and* **4H** (eV) (The experimental values are in parenthesis)

	H–Se–H	H–Se–CH_3	H_3C–Se–CH_3	
Ip_1	9.85 (9.98) [a]	9.22	8.76	(8.40) [b]
Ip_2	12.92	11.92	11.37	(11.0) [b]
Δ	3.07	2.70	2.61	(2.6) [b]

[a] See [23]. [b] See [24].

Table 3. *Energetic Results*

Species	Total energy [a.u.] (Relative energy kcal/mol[a])	HOMO energy [a.u.]	Proton affinity (kcal/mol[b])	3d level energy [a.u.] from[c]	to[d]
1H	– 118.1005	–0.474			
1e	– 117.3804	0.014	452.0		
1a	(0.0)	0.014	452.0		
2H	– 475.9660	–0.340			
2e	– 475.2877	–0.035	426.0		
2a	(6.0)	–0.005	432.0		
3H	–2473.9093	–0.322		–2.671	–2.656
3e	–2473.2363	–0.045	422.5	–2.452	–2.439
3a	(6.4)	–0.017	428.9	–2.448	–2.435
4H	–2434.9261	–0.339		–2.679	–2.664
4e	–2434.2552	–0.042	421.3	–2.449	–2.436
4a	(6.0)	–0.020	427.3	–2.447	–2.434

[a] Total energies of species of type *e*. The values in parenthesis are the relative energies of the species *a* with respect to the corresponding, more stable species of type *e*.

[b] Energy difference between the species listed in the first column and the corresponding protonated derivative.

[c] Energy of the lowest 3d orbital of Se.

[d] Energy of the highest 3d orbital of Se.

Table 4. *Population Analysis on species* **1**–**4**[a])

Species	**1H**	**1e**	**1a**	**2H**	**2e**	**2a**	**3H**	**3e**	**3a**	**4H**	**4e**	**4a**
Overlap Populations: Total (first line); in the HOMO (second line)												
X–C⁻	0.535	0.667	0.623	0.452	0.559	0.359	0.488	0.569	0.391	0.500	0.543	0.392
	0.151	0.038	–0.036	–0.091	0.022	–0.379	–0.068	0.031	–0.342	–0.088	0.007	–0.327
Z–X	0.535	0.441	0.506	0.452	0.338	0.451	0.488	0.393	0.454	0.599	0.477	0.562
	0.151	–0.044	–0.009	–0.091	–0.102	0.003	–0.068	–0.075	–0.037	0.0	–0.080	–0.020
Atomic Populations: Total (first line); in the HOMO (second line)												
⁻C	6.404	6.574	6.578	6.501	6.654	6.666	6.514	6.636	6.646	6.516	6.649	6.657
	0.518	1.811	1.825	0.025	1.782	1.500	0.015	1.766	1.422	0.021	1.807	1.512
X	8.096	8.234	8.250	16.125	16.276	16.298	34.072	34.280	34.308	34.227	34.459	34.484
	0.475	0.048	0.113	1.766	0.057	0.418	1.853	0.067	0.486	1.916	0.078	0.448
Z	8.951	9.123	9.094	8.937	9.118	9.076	8.963	9.140	9.101	0.826	0.948	0.908
	0.759	0.120	0.040	0.117	0.142	0.052	0.074	0.058	0.050	0.0	0.090	0.012
Total Population of the d Functions												
				0.093	0.103	0.099	10.117	10.146	10.134	10.108	10.129	10.125

[a]) X = CH_2 in **1**, S in **2**, Se in **3** and **4**; Z = CH_3 in **1**–**3**, H in **4**.

and more polarisable (4.50 Å^3 [14] than the S atom (3.45 Å^3 [14]) dilutes better the charge formed on C^-. This agrees both with the experimental results on gas-phase acidities and basicities [15] as well as with computational results [1] [2] [16].

Population analysis also provides an illustration of these polarization effects (*Table 4*): the deprotonation adds less charge on the carbon atom when X = Se (0.122–0.132 e) than X = S (0.153–0.165 e) or X = CH_2 (0.170–0.174 e). Comparing now the species **3** H_3C–Se–CH_2^- and **4** H–Se–CH_2^-, one sees that the H_3C–Se group disperses more charge than the H–Se group; however, the protonation energies are in the order ($\Delta \approx$ 1 kcal/mol) opposite to that expected on the basis of these polarization effects alone; we shall come back to this point later.

2. *Stereoelectronic effects.* Like in our previous study [2] one sees that *carbanion stabilization by an α-heteroatom X is conformation dependent*: the equatorial forms **e** are always more stable than the corresponding axial forms **a**. Taking the sp^3 hybridized 1p's of X as a mere orientational indication, one can say that the C–H bond antiperiplanar (app) to this 1p is less acidic than its gauche rotamer. In strong contrast, the two conformations of the propyl anion have the same energy. Although, to our knowledge, there are no experimental results about the stereochemistry of α-seleno carbanions, one can expect effects comparable to those observed in the sulfur case [17]: the energy difference between **2e** and **2a** (6.03 kcal/mol) is comparable to that between **3e** and **3a** (6.40 kcal/mol) or between **4e** and **4a** (6.30 kcal/mol). In the case of α-diseleno carbanions $(SeR)_2CH^-$, this difference should be even larger, about 8 kcal/mol in the gas phase, as in the sulfur case [2].

One can interpret this conformational dependent stabilization in terms of 'anisotropic polarization'; it is nevertheless better represented by hyperconjugative stereoelectronic effects. Although the σ and the p type 1 p's of the heteroatom X are not energetically equivalent [18] our previous studies on stereoelectronic effects in various species [2] [19] have shown that these effects can be interpreted *inter alia* by considering the sp^3 localized 1 p's of X (see discussion in [2]); in the conformations studied, the C^-–1 p may be app to the X–Z bond or to an X–1 p, so that two main interactions occur: (i) in species **e** the two electrons interaction [C^-–1 p, σ^* (X–Z)] is of 'anomeric' type; since it mixes the C^-–1 p with the antibonding orbital of the app X–Z bond, it is stabilizing, strengthens the X–C bond, lengthens the X–Z bond and adds some charge on the Z group; (ii) the four-electrons [C^-–1 p, X–1 p] interaction in species **a** is of reverse anomeric type [20]; since it mixes the C^-–1 p with the app X–1 p, it is destabilizing and weakens the X–C bond.

Most of the results reported in *Tables 3* and *4* agree with this perturbational picture. The HOMO of the anions, which mainly describes the C^-–1 p is more stable in the equatorial forms **2e**–**4c** than in their corresponding gauche rotamer **2a**–**4a**. Taking the overlap population (OP) of a bond as an indication of its strength [21], one observes a weakening of the X–CH_3 bond in the **e** forms with respect to the **a** ones; this difference is less marked in the Se case (ΔOP = 0.061 e) than in the S case (ΔOP = 0.113 e); the X–C^- bond is stronger in the **e** than in the **a** forms, this difference being also less marked in the Se case (ΔOP = 0.178 e for **3e**–**3a**) than in the S case (ΔOP = 0.200 e for **2e**–**2a**). These effects are more pronounced in the HOMO's. The X–Z bond is more polarized in the **e** conformations, with more charge on Z ($\Delta \approx 0.04$ e for **2**–**4**) than in the **a** conformations.

Although the energy difference between the **e** and **a** forms is the same in α-seleno as in α-thia carbanions, the stabilizing interaction (i) seems weaker in the Se case; this may be the result of two opposite factors: the σ^*(Se–CH_3) orbital ($8B_2^*$ of 3H) is lower ($\varepsilon_i = 0.154$ a.u.) than the σ^*(S–CH_3) orbital ($6B_2^*$ of 2H; $\varepsilon_i = 0.191$ a.u.), but the occupied σ(Se–CH_3) orbital is of higher energy ($\varepsilon_i = -0.475$ a.u. for the $7B_2$ MO of **3**) and therefore closer to the C^-–1 p than in the σ(S–CH_3) case ($\varepsilon_i = -0.567$ a.u. for the $5B_2$ MO of **2**). On the other hand, the destabilizing interaction (ii) is stronger in the Se case: the σ and p Se–1 p's are of higher energy (respectively -0.322 and -0.418 a.u. in **3H** than the S–1 p's (respectively -0.340 and -0.435 a.u. in **2H**).

Comparing the anionic species H_3C–Se–CH_2^- (**3**) and H–Se–CH_2^- (**4**), one sees that the protonation energy is lower in **3** than in **4** although the C^- charge is better polarized in **3**. This small energy difference ($\Delta E \approx 1$ kcal/mol) may not be significant especially because of the lack of geometry optimization. This discrepancy may also serve to recall that, although the stereoelectronic effects do exist in the species studied, they do *not* determine *alone* their total energies or their protonation energies⁶). The protonation energies result from a balance between nuclear and different electronic terms, which may be decomposed into specific interactions; the extent to which

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⁶) To illustrate this point, we can notice that the electronic (V_{ee}) and internuclear (V_{NN}) repulsions are always the strongest in the most stable gauche [22] **e** forms (for example $\Delta V_{NN} + \Delta V_{ee}$ amounts to 349.6 kcal for **3e**–**3a**); the contribution of V_{NN} to the protonation energy also differs very much from one species to another (for example, $\Delta V_{NN} = 6705$ kcal/mol for **4H** → **4a**, and $\Delta V_{NN} = 7544$ kcal/mol for **3H** → **3a**!).

some of them may be said to dominate is less clear than the identification of specific effects[7]).

3. *The effect of the d orbitals of Se.* Previous calculations on **2** with and without d functions on the S atom showed that α-thia carbanions are not stabilized by $(d\text{–}p)_\pi$ conjugation; the d functions stabilize the anions **2e** and **2a** by the same amount as the conjugated acid **2H** and therefore do not affect the protonation energy [2]. In the case of selenium, this procedure is not possible since the 3d level of Se is fully occupied; the following discussion on the role of the d functions of Se will then rely on orbital analysis and population analysis results. Two types of interactions between the C^-–1p and the d orbitals of Se can be considered: the first one with the fully occupied $3d^{10}$ level of Se is repulsive, the second one with the empty 4d level of Se is attractive. We will see that these interactions are very weak in compounds **3**, **4** and SeH_2 and should not affect the protonation energies. The d orbitals of Se are essentially core orbitals whose energy (≈ -2.5 a.u.) is much lower than the valence levels and which do not mix with other orbitals. Their energy spreads over about 0.3 eV in the charged as well as in the neutral species[5]). One may compare their evolution from one molecule to another, taking as reference SeH_2, which has the most stable d levels (-2.768 to -2.692 a.u.) and the least populated d functions (10.099 e); substitution of the H atom by a methyl group has a destabilizing effect of about 0.3 eV and raises the total population of the d functions (d–Pop) by about 0.01 e. The negative charge formed by deprotonation of **3H** and **4H** destabilizes these d levels by about 6 eV, somewhat more in the **a** forms than in the **e** forms ($\Delta \approx 0.08$ eV), indicating weak repulsive effects in the anions. Looking now at the population analysis results, one sees that the total population of the first contracted d_1 function is the same in all seleno compounds SeH_2, **3** and **4**, (9.932 e); this illustrates again its use for the core description. The small variations of d-Pop are than due to the more diffuse d_2 function, more populated in the **e** forms than in the **a** forms ($\Delta = 0.012$ e for **3e**–**3a**, $\Delta = 0.004$ e for **4e**–**4a**), like the d functions of S in the sulfur compounds ($\Delta = 0.004$ e for **2e**–**2a**). The comparison between the Se and S case also shows that the increase of the d-Pop by deprotonation is more important in the Se case ($\Delta \approx 0.02$ e for **3** and **4**) than in the S case ($\Delta \approx 0.008$ for **2**), so that the 4d-Pop of Se should be slightly higher (0.117 e in **3H**, 0.146 e in **3e**) than the 3d-Pop of S (0.093 e in **2H**, 0.103 e in **2e**); although weak these differences suggest a better stabilizing interaction between C^- and the empty 4d orgitals of Se than with the 3d orbitals of S. Whether such stabilization, and its eventual effect on protonation energies, should be ascribed to slightly better $(d\text{–}p)_\pi$ bonding in seleno-carbanions is a mere matter of taste; such weak d participation may be more simply included into the polarization effects.

Conclusion. – The present *ab initio* study on α-seleno carbanions has shown that they are more stable than the corresponding α-thia carbanions by about 3 kcal/mol. This stabilization is related to the greater polarisability of the Se atom compared

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[7]) We have previously shown that in $CH(OH)_2NH_2$ the conformations which show strongest 1p–σ^* (C–X) interactions may not be the most stable ones. Dipole-dipole, bond-bond interactions, *etc.* also contribute markedly to total energies. The question as to which effect *explains* properties like the anomeric or anti-anomeric effects, is better considered as that of which effect may *dominate* in a specific compound.

to the S atom. Strong stereoelectronic effects are found; the **e** forms are appreciably more stable than the **a** forms and this **e–a** difference is about the same as in α-thiacarbanions. The d orbitals of Se are mainly core orbitals, without any specific effect on the α-seleno-carbanion stability.

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