Are there Anomeric Effects involving Selenium?

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The preferred C_2 conformation of $CH_2(SeH)_2$, the total stabilization energy (8.1 kJ mol^{-1}) evaluated from the isodesmic equation (1), and the favourable 3p(Se)–σ^*(C–Se) orbital interaction are in accord with weak negative hyperconjugation.

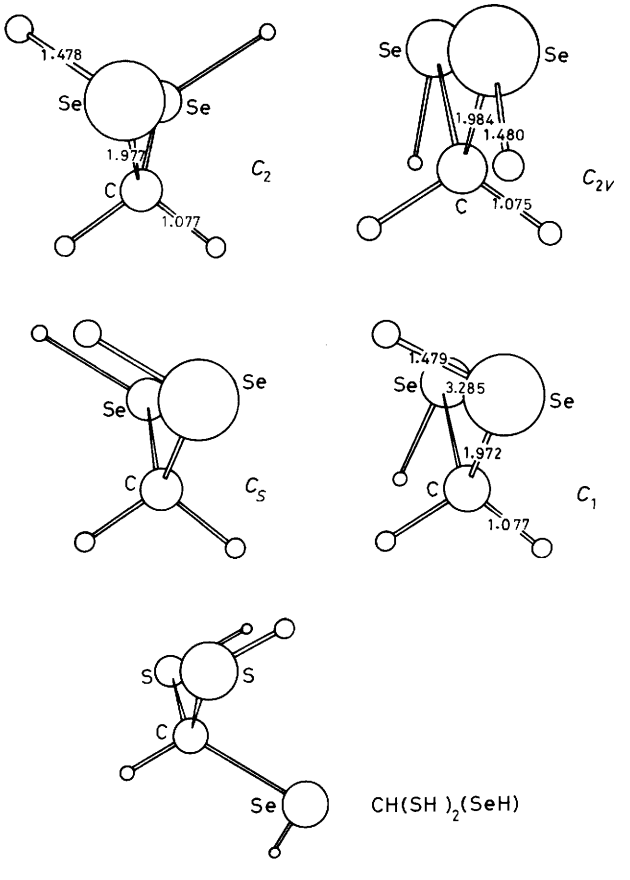
Pinto *et al.* recently called attention to unusual solid-state conformations of a selenium coronand.[1] The *gauche,gauche* Se–C–Se arrangements in 1,3,7,9-tetraselenacyclodecane and its 5,5,11,11-tetramethyl derivative were attributed to anomeric effects[2] and the conformational equilibrium of 2-[(4-methoxyphenyl)seleno]-1,3-dithiane in polar solvents were explained in terms of a double-bond no-bond structure.[3]

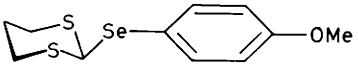
Negative hyperconjugation[4] is found in XCH_2Y systems when X is an electronegative substituent and Y is a good π donor.[5] The σ^*(C–X) orbital is lowered in energy and

Table 1. Selected geometrical parameters, absolute energies, zeropoint energies (ZPE), and energies for the isodesmic reaction [equation (1)].

Species	Symmetry	R(C–Se) /Å	R(C–H) /Å	θ(H–C–Se)/°	θ(Se–C–Se)/°	E /a.u.	ZPE /kJ mol^{-1}	ΔE^{a} /kJ mol^{-1}
CH_4	T_d		1.084			−40.35329	125.3	
CH_3SeH	C_s	1.985	1.078	96.5		−2438.01469	124.2	
			1.080					
$CH_2(SeH)_2$	C_2	1.977	1.077	96.4	117.4	−4835.67805	119.8	8.1
	C_1	1.972	1.077	96.2	112.2	−4835.67687	119.4	5.3
		1.985	1.076	95.8				
	C_s	1.977	1.076	96.2	118.0	−4835.67660	119.0	5.0
			1.078					
	C_{2v}	1.984	1.075	95.9	108.1	−4835.67387	118.5	−1.7

[a] MP4SDTQ/6-31G*(Se–Hu)//HF6-31G*(Se–Hu) + ZPE.





(A)

Figure 1

polarized more towards C, hence the larger π-overlap allows better Y lone pair delocalization into this orbital.[5] Theoretical investigations have shown that negative hyperconjugation tends to diminish when second row elements are involved owing to their decreasing electronegativity (as X) and their lower π-donor ability (as Y).[5] Sulphur, selenium, and carbon have nearly the same electronegativity according to most scales.[6] Since the σ-acceptor character of a substituent is directly related to its electronegativity,[7] hyperconjugation should be unimportant in selenium systems.[5]

We examined the conclusions of Pinto *et al.* theoretically at MP4SDTQ/6-31G*(Se–Hu)//HF6-31G*(Se–Hu) + ZPE level.[8] Since no 6-31G* Se basis is available, we used Huzinaga's 43321/431/4 split valence basis set.[9] In order to check whether basis set balance was achieved, the most stable (C_2) structure was reoptimized twice: first using Huzinaga's 421/31 basis for carbon instead of 6-31G* and then mixing 6-31G* for carbon with the 43321/4321/311* polarized split valence basis for Se. We calculated different conformations (Figure 1) of $CH_2(SeH)_2$ for comparison with other X–CH_2–Y systems, where X and Y are first[7]- and second[5]-row substituents. By using such isolated units we avoid additional effects such as ring constraints or solid-state and solvent interactions. We stress that the evidence given by Pinto *et al.* is indirect. Hyperconjugative interactions between the substituents may be examined directly by evaluating group separation reactions[8] [equation (1)] and by calculating the energy gain from orbital interactions by analysing the Fock matrix.[10] The total stabilization energy can be evaluated by the isodesmic reaction (1).[8]

$$CH_2(SeH)_2 + CH_4 \rightarrow 2CH_3SeH \qquad (1)$$

The stabilization energy for the most stable conformation (C_2) was found to be only 8.1 kJ mol^{-1} at the MP4SDTQ/6-31G*(Se–Hu)//HF6-31G*(Se–Hu) + ZPE level. For X, Y = OH and SH the stabilizations at MP3/6-31G*//6-31G* level are 66.0 and 5.9 kJ mol^{-1} respectively.[11] The C_s and C_2 symmetry structures of $CH_2(SeH)_2$ are equivalent,[12] with respect to hyperconjugation, and the stabilization of the former is 5.0 kJ mol^{-1}.

There are two possible hyperconjugative interactions: 3p(Se)–σ*(C–Se) and 3p(Se)–σ*(C–H). The first interaction favours the C_2 conformation and the second C_{2v} because the strongest effect involves the lone pair aligned parallel with the acceptor orbital.[11] The C_{2v} conformation (a transition state on the potential energy surface) is destabilized by −1.7 kJ mol^{-1} according to equation (1). A C_1 structure, which has both a *trans* and a *gauche* conformation also is a minimum and has a stabilization energy of 5.4 kJ mol^{-1}.

The stabilization energy depends on the ratio between the square of S_{ij}, the overlap matrix element, and ΔE_{ij}, the energy difference between the interacting orbitals.[13] The elements of the Fock matrix F_{ij} and S_{ij} are roughly proportional to each other and generally of the same order of magnitude.[14] These ΔE_{ij} values and Fock matrix elements can be evaluated by the

'Natural Bond Orbital Analyses' program.[10] The 3p(Se)–σ*(C–Se) interaction for C_2 symmetry is stabilizing by 35.4 kJ mol^{-1} whereas the 3p(Se)–σ*(C–H) interaction leads to an energy gain of 9.2 kJ mol^{-1} due to a smaller F_{ij} and a larger ΔE_{ij}. The difference is somewhat larger for C_s symmetry, the values being 38.7 and 7.8 kJ mol^{-1}, respectively. For C_{2v} symmetry where no 3p–σ*(C–Se) interaction is possible, there are two 3p–σ*(C–H) interactions with a stabilization energy of 13.9 kJ mol^{-1}. For comparison, the energy gain in F_2CH_2 (a molecule exhibiting strong negative hyperconjugation) is 88.6 kJ mol^{-1} due to the p–σ* interaction.[14]

The bond lengths of the C_2 and C_s forms are not easy to predict: donation from the π-orbital should shorten the Se–C bond whereas donation into the σ*-orbital should have the opposite effect. Table 1 shows a bond length contraction in the C_2 and C_s structures, which have the same Se–C bond lengths. But the decrease of 0.008 Å compared to CH_3SeH is much less than in $CH_2(OH)_2$ where the C–O bond is shortened by 0.020 Å compared to CH_3OH.[12] In the C_1 structure one bond is 0.005 Å shorter than in the C_2 structure but the other bond has the same value as in CH_3SeH. Neither a stabilizing interaction nor a bond length contraction is present in the C_{2v} form.

The only geometrically significant effect is the widening of the Se–C–Se angle. The repulsion between the lone pair orbital and the σ(C–Se) as well as σ*(C–Se) orbital is decreased as the Se–C–Se angle is increased. This leads to stronger overlap and thus to a higher stabilization energy.[15] These angles, 117.4 and 118.0° for the C_2 and C_s structures, respectively, are much wider than tetrahedral and even wider than the O–C–O angle (112.4°) in $CH_2(OH)_2$ (C_2).[12] For comparison, the Se–C–Se angle in C_{2v} symmetry is 108.1°. The C_1 bond angle is 112.2°.

The same trend in going to lower rows is observed with silicon systems.[11] The interaction energies and bond length contractions decrease but the X–C–Y bond angles become wider. Are steric effects responsible as proposed by Wiberg and Murcko for dimethoxymethane?[16] The Se–Se distance is only 3.38 Å and the Se atoms are more bulky than O. Several single point calculations with bond angles varying from 108 to 116° were carried out. For each structure the hyperconjugative interactions were suppressed by deleting the corresponding Fock matrix elements. Then one SCF cycle was performed to obtain the energies in the absence of anomeric effects.[10] This procedure results in an energy minimum near 110°. A 7.5 kJ mol^{-1} energy difference is found between the structures with Se–C–Se angles of 110 and 117.4°. The energy loss by deleting the hyperconjugative interactions is 51.5 kJ mol^{-1} for the 117.4° and 37.7 kJ mol^{-1} for the 110° structure. Hence, the bond angle widening is due to the 3p–σ*(Se–C) orbital interaction.

Pinto *et al.* proposed a double-bond no-bond structure with a negatively charged selenium for the axial conformation of 2-[(4-methoxyphenyl)seleno]-1,3-dithiane (**A**). They also interpreted the measured dipole moments in the equatorial and axial structure by attributing a negative charge to selenium.[3] In all our calculations, selenium is positively charged, even when sulphur and selenium are bound to the same carbon centre. Selenium is positive in $C(SH)_2(SeH)H$, examined in a conformation akin to that found in the experimental system (Figure 1). The main orbital interactions are 3p(S)–σ*(C–S), 3p(Se)–σ*(C–S), 3p(Se)–σ*(C–H), and 3p(S)–σ*(C–Se). The relative order in magnitude depends on the H–C–S–H angle but in all cases we found that the stabilization is stronger if selenium acts as the π-donor and sulphur as the σ-acceptor: [3p(Se)–σ*(C–S)] rather than [(3p(S)–σ*(C–Se)]! In addition, selenium π-donates into the adjacent C–H antibond.

Despite the fact that selenium and carbon have nearly the same electronegativities, the trends in bond angles, bond lengths, and total energies of different conformations of $CH_2(SeH)_2$ are in accord with weak negative hyperconjugation. However, the stabilization energy evaluated by the group separation reaction is nearly eight times less and the bond length contraction is three times less than for $CH_2(OH)_2$. Only the bond angle widening, which is not directly related to the strength of the anomeric effect, is significant. Thus, hyperconjugation is expected to be only one of several factors that influence the actual conformation of the larger systems.

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