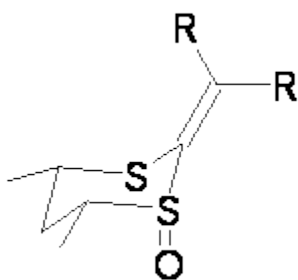


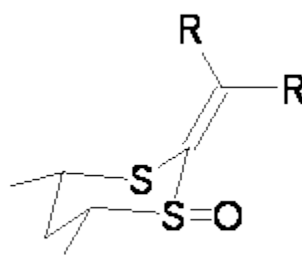
CONFORMATIONAL PREFERENCE IN VINYL SULFOXIDES

The conformational preference of α - β -unsaturated carbonyl compounds is well established: the two π -bonds prefer to be in conjugation with the oxygen and three carbon atoms (nearly) coplanar. Now, what about the conformational preference of vinyl sulfoxides? Since the S-O π -bond is weak, alternate conformations might be favorable. Podlech has prepared some 1,3-dithiane-1-oxides that should be conformationally static and thereby offer some insight into this question.¹ The dithiane oxides **1** and **2** can exist with the S-O bond in the axial (**a**) or equatorial (**e**) positions.



1a: R=H

2a: R=Me



1e: R=H

2e: R=Me

The B3LYP/6-31++G(d,p) geometries are shown in Figure 1. The equatorial structure has the two π bonds close to coplanar (the C-C-S-O dihedral is 14°), while in the axial isomers, the C-C-S-O dihedral is about -122° .

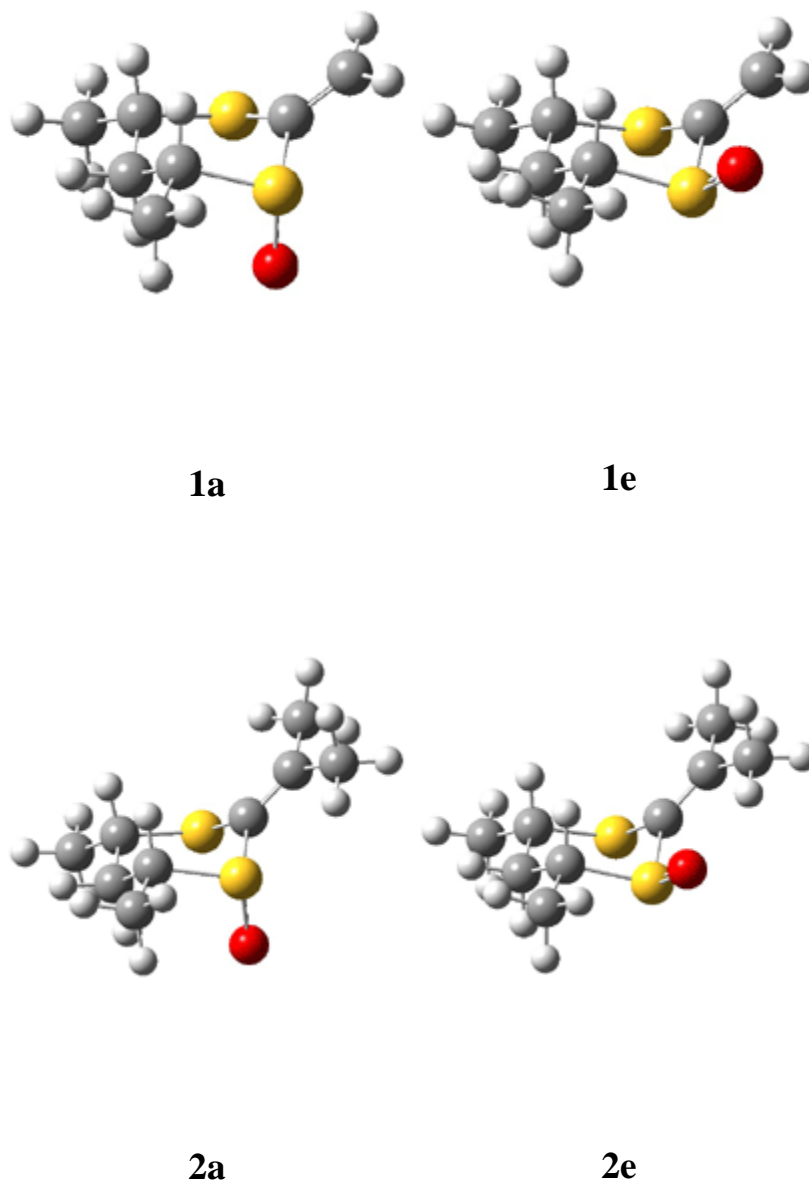


Figure 1. B3LYP/6-31++G(d,p) optimized structures of **1** and **2**.

Podlech argues for a $\pi_{C=C} \rightarrow \sigma^*_{S-O}$ stabilization in the axial isomer on the basis of two observations. First, the UV maximum absorbance in **1a** is at 266nm, 12 nm greater than in **1e** and similarly, the UV maximum in **2a** is 2 nm higher than in **2e**. Second, NBO analysis indicates a much larger contribution for this interaction in **1a** (3.05 kcal mol⁻¹) than in **1e** (0.07 kcal mol⁻¹).

However, I am unconvinced that this interaction is really dominant. Oxidation of the precursor dithiane with MCPBA gives a 42:58 ratio of **1e:1a** and a 76:24 ratio of **2e:2a**, which indicates a preference for the equatorial form of **1** and only a small preference for the axial form of **2**. Unreported by Podlech (even in the supporting materials) is the relative computed energy difference of the two stereoisomers. At B3LYP/6-31++G(d,p) with ZPE, **1e** is 2.6 kcal mol⁻¹ lower in energy than **1a** and **2e** is 0.05 kcal mol⁻¹ lower than **2a**. So, in the gas-phase, it appears that the vinyl sulfoxides prefer the equatorial orientation, just as in α - β -unsaturated carbonyl compounds. The $\pi_{C=C} \rightarrow \sigma^*_{S-O}$ interaction is stronger in the axial conformation, but it is doubtful that this alone manifests in any diastereomeric selectivity.

Source: <http://comporgchem.com/blog/?p=637>