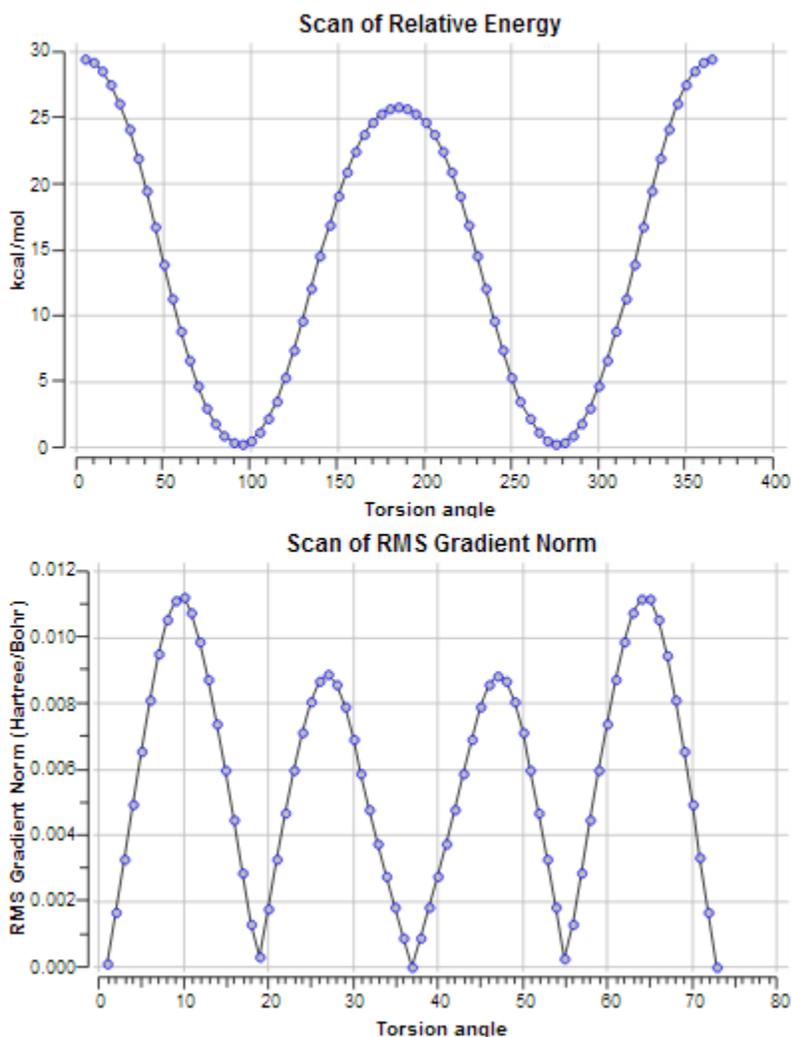


An example of an extreme gauche effect: FSSF

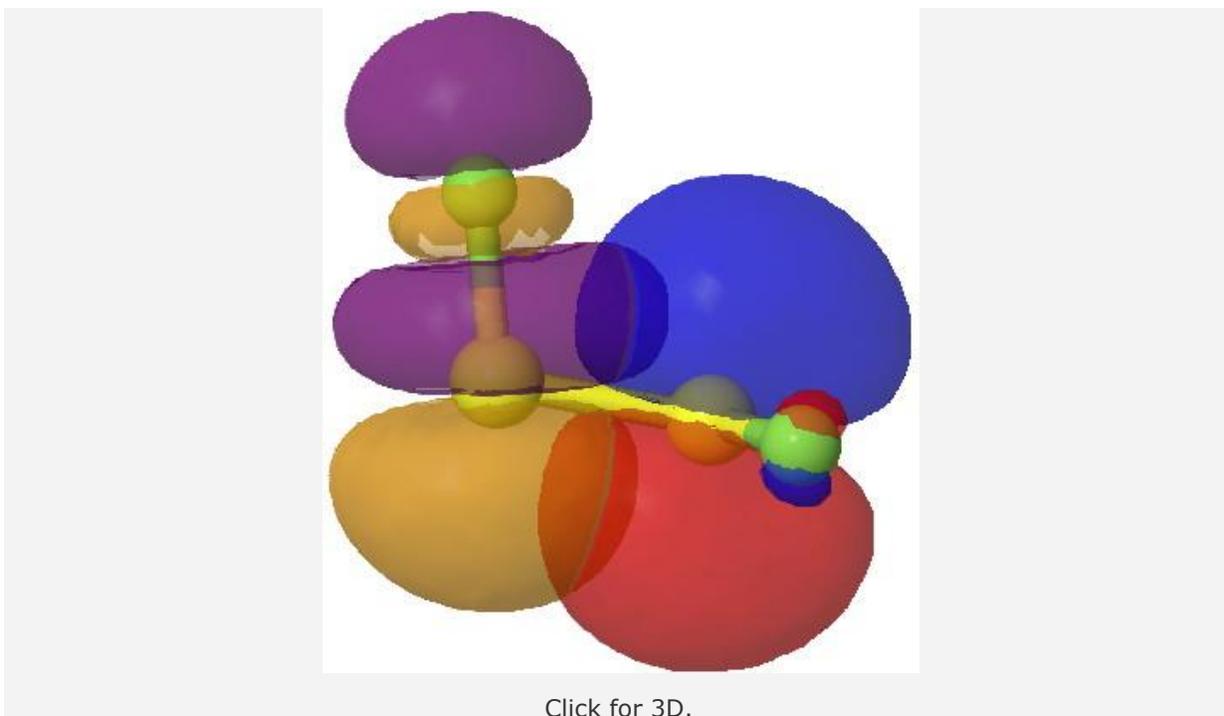
The best known example of the *gauche* effect is [1,2-difluoroethane](#), which exhibits a relatively small preference of ~ 0.5 kcal/mol for this conformer over the *anti* orientation, which is also a minimum. But FSSF, which I discussed in the [previous post](#), beats this hands down! It also, by the way, must surely be the smallest molecule (only four atoms) which could be theoretically resolved into two enantiomers (possibly at say 273K?).[‡]



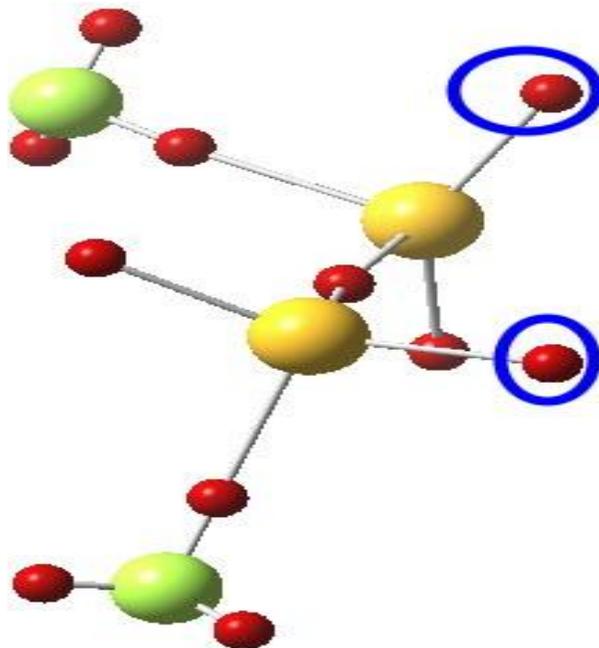
From this optimised scan[1] of the F-S-S-F torsion angle, you can see two striking differences

1. Only the *gauche* form is stable. The *anti* form is in fact a transition state[2] for enantiomerisation of the two chiral C_2 -disymmetric *gauche* forms.

- The difference in free energy between the gauche form and the anti is 25.3 kcal/mol, compared with which the 0.5 kcal/mol for 1,2-difluoroethane looks puny indeed.
- The effect arises, as with difluoroethane, from overlap of the filled p-lone pair on one sulfur, with the accepting S-F σ^* orbital.



- This orbital overlap results in an NBO E(2) interaction energy of 39 kcal/mol. This compares with 5.6 kcal/mol for the equivalent C-H/C-F* term for difluoroethane, and it is of course larger because an S lone pair is a far better donor than a C-H bond. It is also far greater than the anomeric effect, which normally weighs in at about 16 kcal/mol.
- There is of course an alternative (and perhaps more unusual) transition state^[3] for interconverting the two enantiomers of F-S-S-F which I [described previously](#) for F-S-S-Cl as involving a [1,2] migration of F. It however is 23.5 kcal/mol higher in energy than this pure bond rotation. Whereas the [1,2] F migration contracts the S-S bond at the transition state, the bond rotation lengthens it (from 1.922 to 2.142Å). This arises because the partial double bond character for the S-S bond is destroyed by rotation. The challenge then is whether one can find a 4-atom system where enantiomerisation proceeds by a lower energy continuously-chiral [1,2] migratory pathway rather than just by a simple bond rotation.
- An alternative visualisation of the electronic effects resulting in an extreme *gauche* effect can be seen from the ELF analysis^[4] of the lone pair basins;



7. The two basins ringed in blue (2.25e) are each aligned at an angle of 167° to the axis of the antiperiplanar S-F bond. The knock-on effect of this is that the two lone pairs on each sulfur themselves subtend an unusual angle of 145° at the common sulfur, almost diaxial in fact.

I again marvel at how just four atoms and just two elements, can teach us so much chemistry!

References

1. Henry S. Rzepa., "Gaussian Job Archive for F2S2", 2013.<http://dx.doi.org/10.6084/m9.figshare.804328>
2. Henry S. Rzepa., "Gaussian Job Archive for F2S2", 2013.<http://dx.doi.org/10.6084/m9.figshare.805048>
3. Henry S. Rzepa., "Gaussian Job Archive for F2S2", 2013.<http://dx.doi.org/10.6084/m9.figshare.802815>
4. Henry S. Rzepa., "Gaussian Job Archive for F2S2", 2013.<http://dx.doi.org/10.6084/m9.figshare.804332>

Source: <http://www.ch.imperial.ac.uk/rzepa/blog/?p=11279>