



A visualization of the anomeric effect from crystal structures.

HENRY RZEPA

READ REVIEWS

WRITE A REVIEW

CORRESPONDENCE:

h.rzepa@imperial.ac.uk

DATE RECEIVED:

September 13, 2015

DOI:

10.15200/winn.144212.25640

ARCHIVED:

September 13, 2015

CITATION:

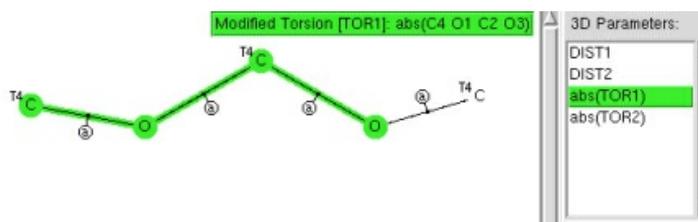
Henry Rzepa, A visualization of the anomeric effect from crystal structures., *The Winnower* 2:e144212.25640, 2015, DOI: 10.15200/winn.144212.25640

© Rzepa This article is distributed under the terms of the [Creative Commons Attribution 4.0 International License](#), which permits unrestricted use, distribution, and redistribution in any medium, provided that the original author and source are credited.



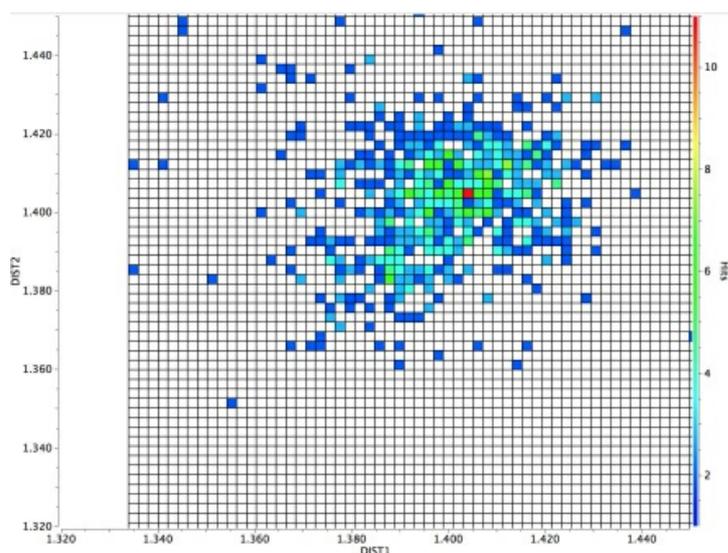
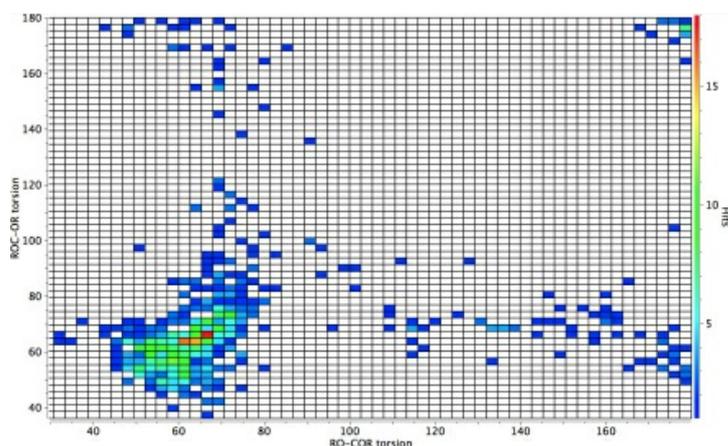
0000-0002-8635-8390

The **anomeric effect** is best known in sugars, occurring in sub-structures such as RO-C-OR. Its origins relate to how the lone pairs on each oxygen atom align with the adjacent C-O bonds. When the alignment is 180° , one oxygen lone pair can donate into the C-O σ^* empty orbital and a stabilisation occurs. Here I explore whether crystal structures reflect this effect.

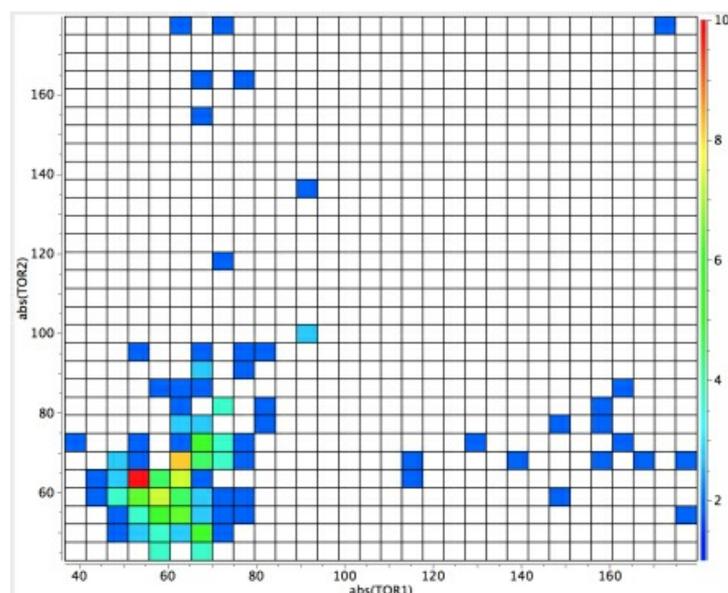


The torsion angles along each O-C bond are specified, along with the two C-O distances. All the bonds are declared acyclic, and the usual $R < 5\%$, no disorder and no errors specified.

1. You can see from the plot below that the hotspot occurs when **both** RO-CO torsions are $\sim 65^\circ$. From this we will assume that the two (unseen)[†] lone pairs at any one of the oxygens are distributed approximately tetrahedrally around each oxygen, and if this is true then one of them must by definition be oriented $\sim 180^\circ$ with respect to the same RO-CO bond (the other is therefore oriented -60°). This allows it to be antiperiplanar to the adjacent C-O bond and hence interact with its σ^* empty orbital. So the hotspot corresponds to structures where BOTH oxygen atoms have lone pairs which interact with the adjacent O-C anti bond.
2. There is a tiny cluster for which **both** RO-CO torsions are $\sim 180^\circ$ and hence neither oxygen has an antiperiplanar lone pair.
3. Only slightly larger are clusters where one torsion is $\sim 65^\circ$ and the other $\sim 180^\circ$, meaning that only one oxygen has an antiperiplanar lone pair.
4. A plot of the two C-O lengths indeed shows an overall hotspot at $\sim 1.40\text{\AA}$ for both distances. If the search is filtered to include only torsions in the range $150\text{--}180^\circ$, the hotspot value increases to 1.415\AA for both. If one torsion is restricted to $40\text{--}80^\circ$ and the other to $150\text{--}180^\circ$ the hotspot shows one C-O bond is about 0.012\AA shorter than the other.

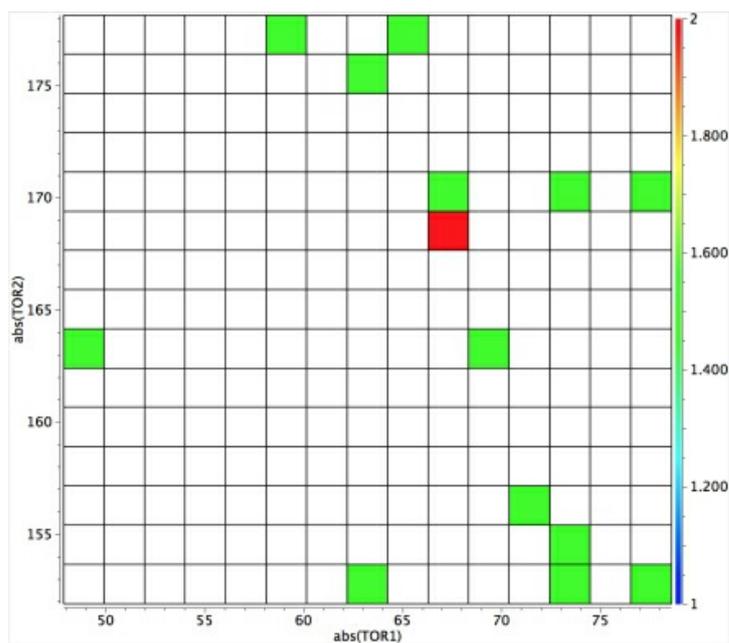


I also include a further constraint, that the diffraction data must be collected below 140K. The hotspot moves to $\sim 55/60^\circ$ indicating values free of some vibrational noise.



Interestingly, replacing oxygen with nitrogen reveals relatively few examples of the effect ($C(NP_2)_4$ is an exception). Replacing O by divalent S produces only 13 hits, with the surprising result (below) that in all of them only one S sets up an anomeric interaction. Arguably, the number of examples is too low

to draw any firm conclusions from this observation.



‡Most diffractometers measure low angle scattering of X-rays by high density electrons. These are the core electrons associated with a nucleus rather than the valence electrons associated with lone pairs. Hence very few positions of valence lone pairs have ever been crystallographically measured.