the WINNOWER

CHEMISTRY

The gauche effect: seeking evidence by a survey of crystal structures.

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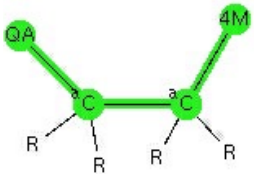
DATE RECEIVED:
June 10, 2015

DOI:
10.15200/winn.142795.55871

ARCHIVED:
April 02, 2015

CITATION:
Henry Rzepa, The gauche effect: seeking evidence by a survey of crystal structures., *The Winnower* 2:e142795.55871 , 2015 , DOI: 10.15200/winn.142795.55871

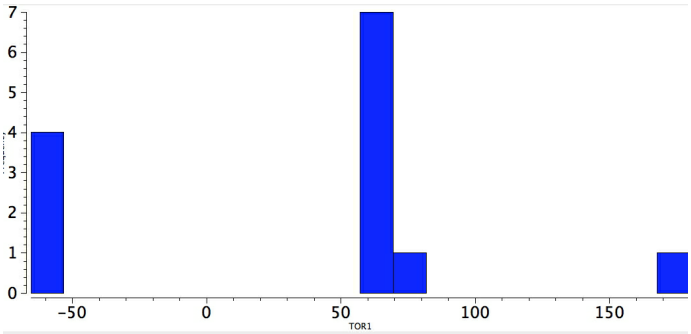
I previously blogged about anomeric effects involving π electrons as donors, and my post on the conformation of 1,2-difluorethane turned out one of the most popular. Here I thought I would present the results of searching the Cambridge crystal database for examples of the ***gauche effect***. The basic search is defined below



Defined Torsion [TOR1]: QA1 C2 C3 4M4

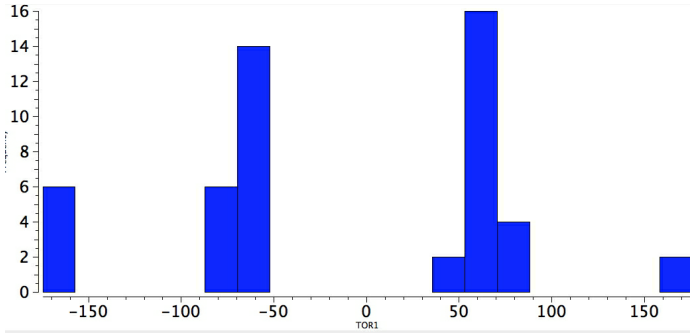
Here, we define a four-atom torsion (TOR1), the two central carbon atoms having two groups R which can be only H or C. These two carbons are also defined as ***acyclic***. The restrictions of the search as defined above also include R-factor < 0.05, not disordered and no errors. These combine to reduce the number of hits significantly (although not dissimilar distributions are obtained for less restricted searches). Each search takes only a few seconds, and one can rattle through many permutations very quickly.

So here come the results. First, QA=4M=F. All but one of the examples has a torsion in the region of 60°, the classic gauche effect!



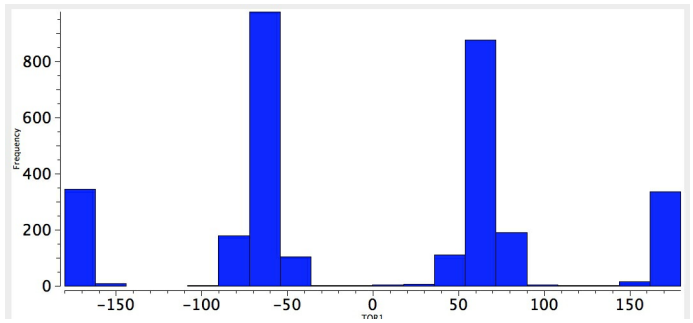
F-C-C-F

Next, QA=O, 4M=F. Rather more hits, and the effect is almost as clear-cut. I should point out that the apparent “exceptions” to the gauche conformation may arise from structural restrictions, and each really would have to be inspected individually for the reasons (which I do not attempt here).



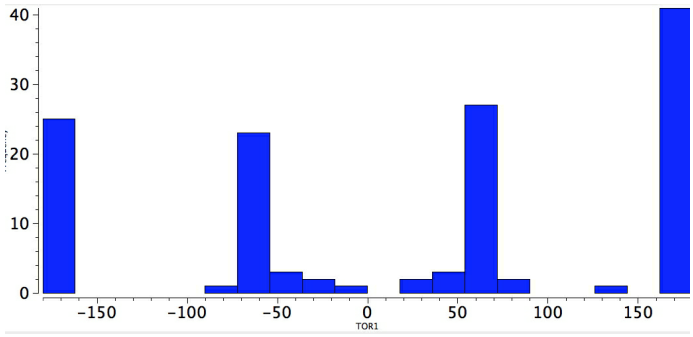
OCCF

With QA=4M=O, one has many more instances. The effect is pretty convincing (it may be that hydrogen bonding may also control the conformation).



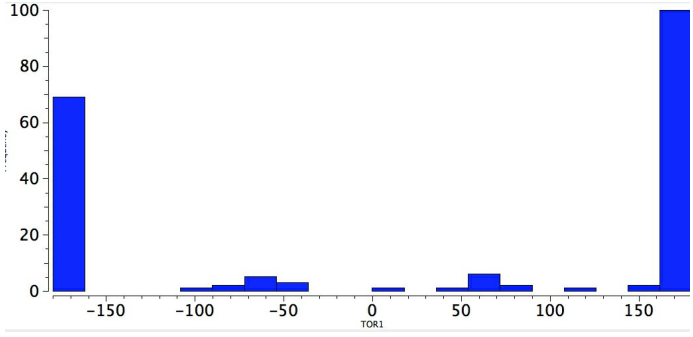
O-C-C-O

Now for QA=4M=Cl. The distribution is slanted more to the anti conformation, but there are still quite a few gauche.



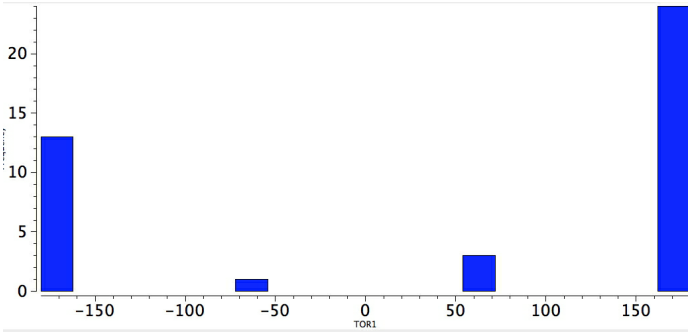
Cl-CC-Cl

With QA=4M=S, the conformations are now almost all anti; the gauche effect is no more!



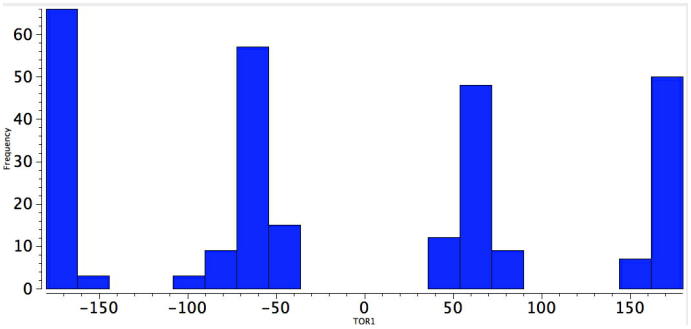
S-C-C-S

And for QA=4M=Br, it has also almost vanished (there is only one instance for I, and that too is antiperiplanar).



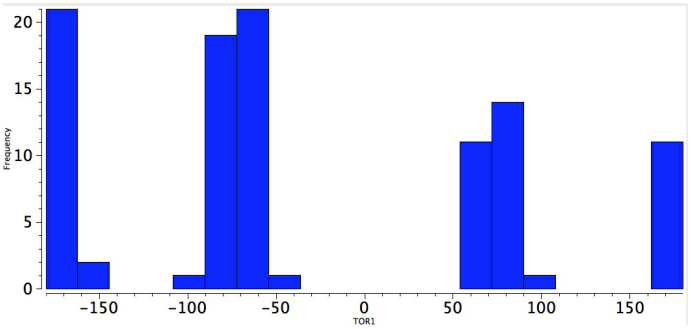
Br-C-C-Br

I now return to an earlier post in which I speculated that a cyano group might participate in the anomeric effect. Well here it is in the gauche effect; QA=CN, 4M = any of N,O,F,Cl,S. Quite a few gauche orientations for this pseudo-halogen!

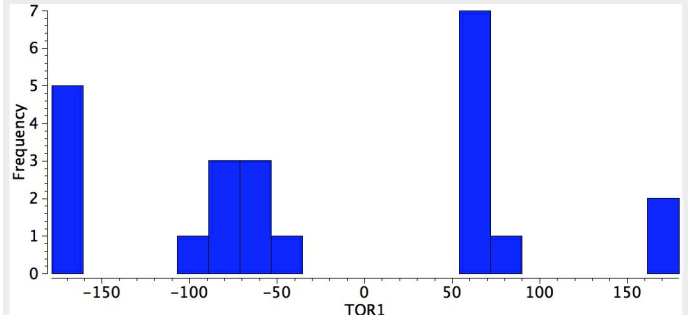


Neg-C-C-CN

Another group that can act as a powerful acceptor of electrons from a donor is QA=N(Me)3$^{+\cdot}$. With 4M= N, O, F, Cl, here the population of gauche conformers is large. QA=CF3 is a similar group.

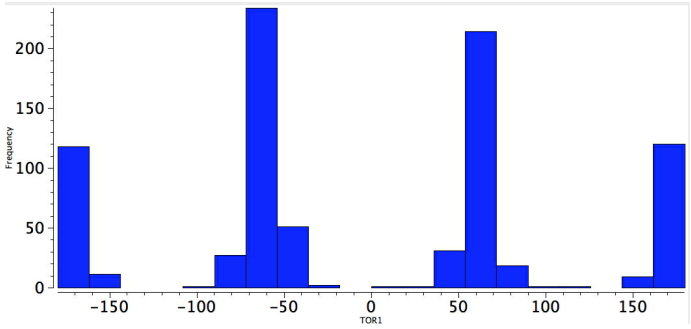


Neg-C-C-NMe3



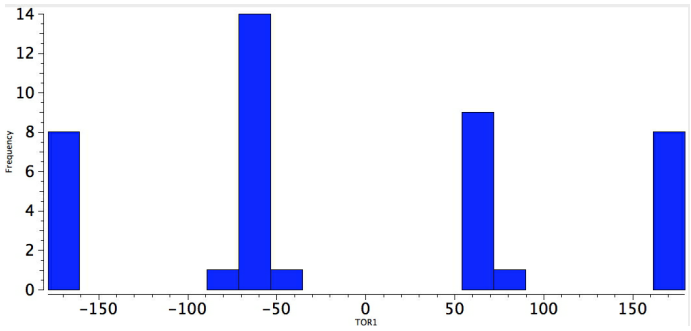
Neg-C-C-CF3

One can envisage other combinations. Thus QA= C=C, 4M = any of N, O, F, Cl. An alkene seems one of the more powerful gauche effect participants!



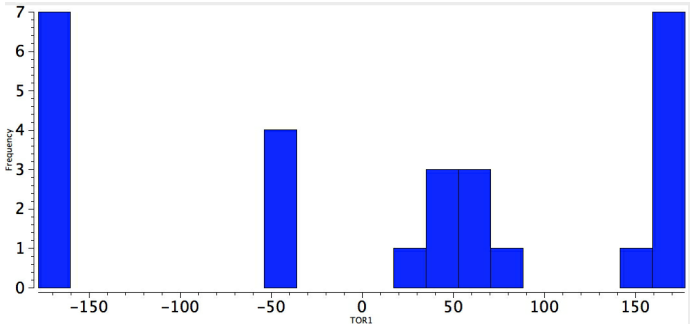
alkene-C-C-Neg

And alkynes, perhaps slightly less so.



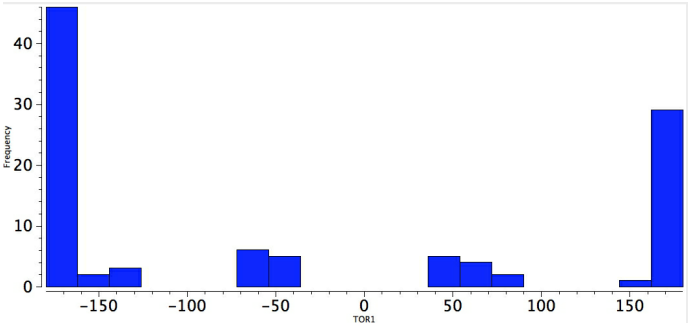
Alkyne-C-C-Neg

What about metals (QA = any metal, 4M = any of N, O, F, Cl, S). Well, not particularly biased either way, but clearly one in which the identity of the metal may matter.



Metal-C-C-electronegative

I should end with inverting the model. If QA is electropositive (any group to the left of carbon, or below it in the periodic table) and 4M is electronegative, than they align almost exclusively anti-periplanar and not gauche. But notice how relatively few examples there are. Synthetic chemists, please make more such molecules!



Electropositive-C-C-Electronegative

If you thought the gauche effect was restricted to just a few molecules, think again!