



A visualisation of the effects of conjugation; dienes and biaryls.

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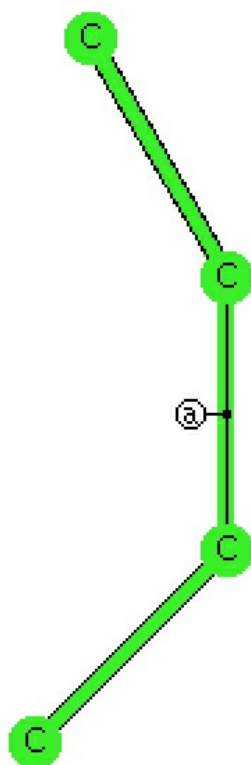
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Here is another exploration of simple chemical concepts using crystal structures. Consider a simple diene: how does the central C-C bond length respond to the torsion angle between the two C=C bonds?

Modified Torsion [TOR1]: $\text{abs}(\text{C4 C3 C2 C1})$



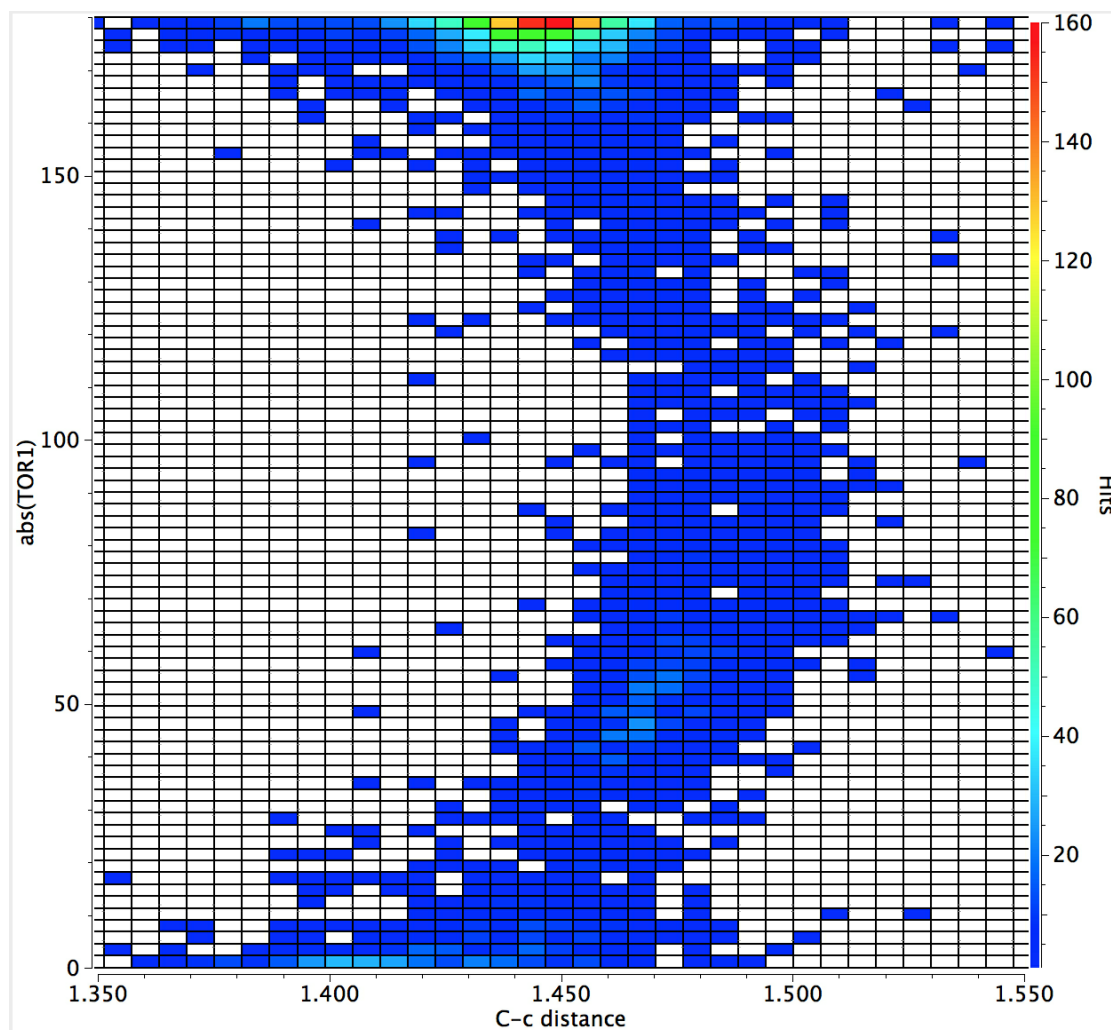
3D Parameters:

DIST1

$\text{abs}(\text{TOR1})$

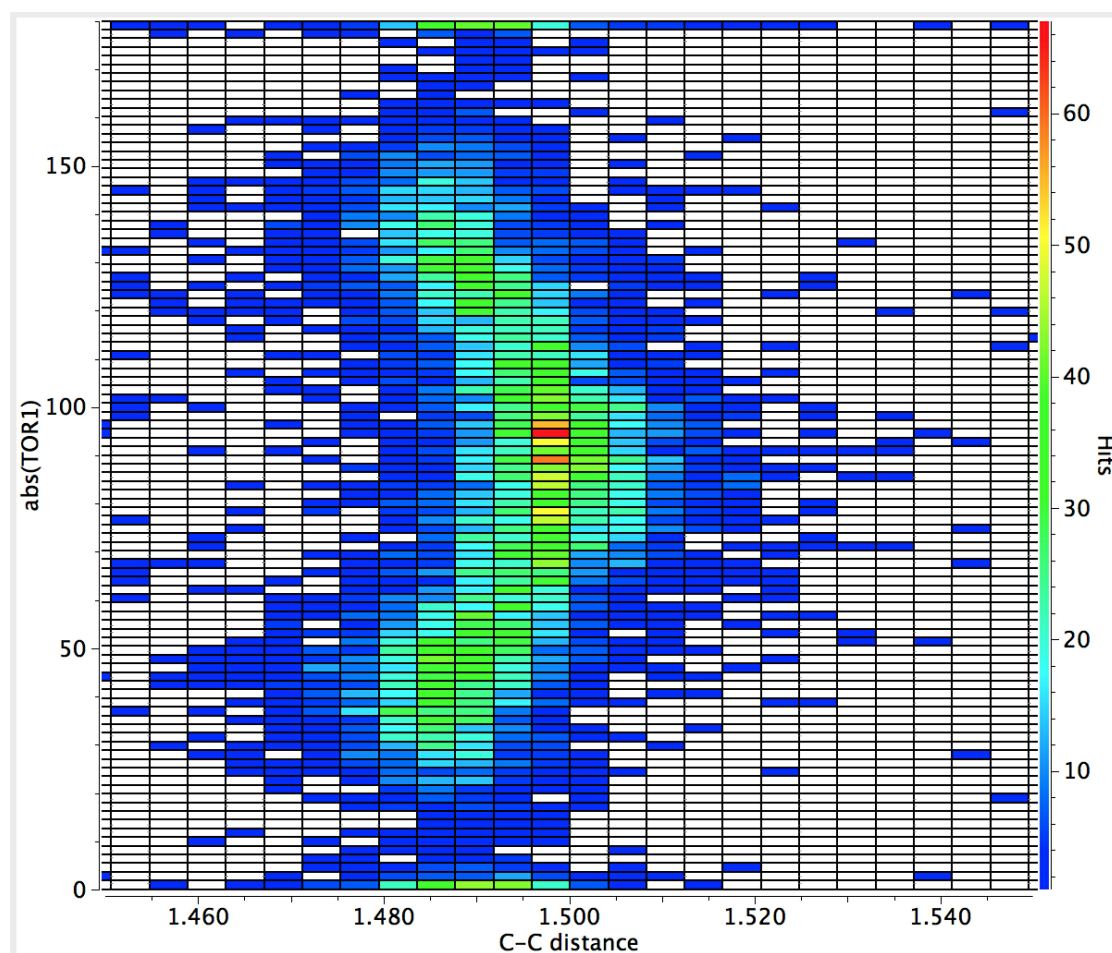
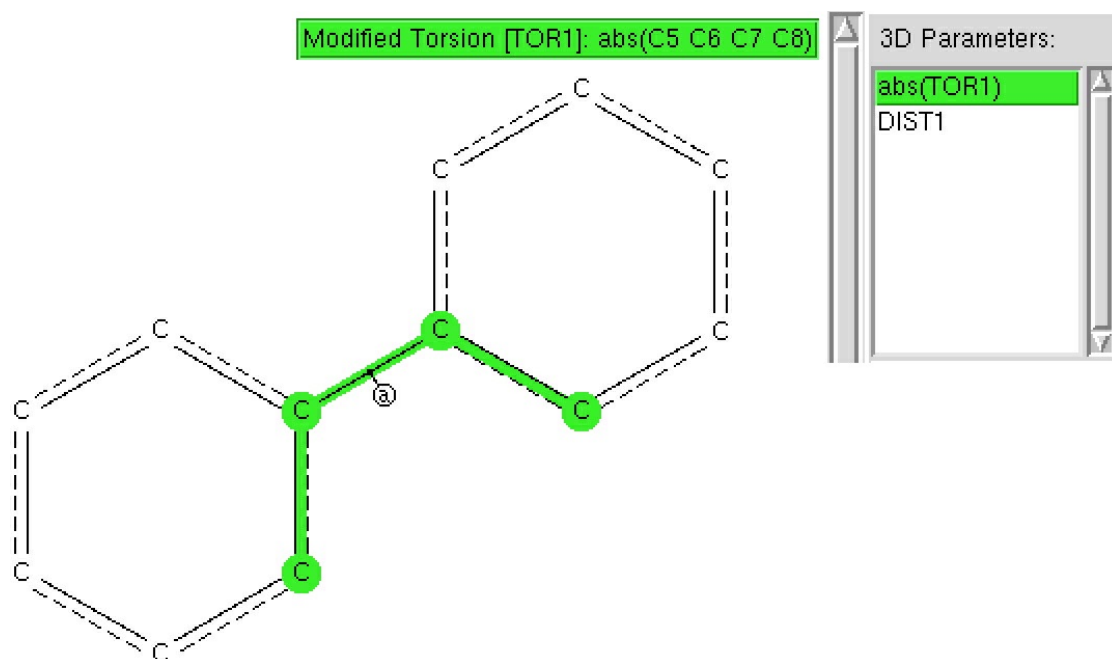
DIST2

The search of the CSD (Cambridge structure database) is constrained to $R < 5\%$, no errors and no disorder and the central C-C bond is specific to be acyclic. [‡]



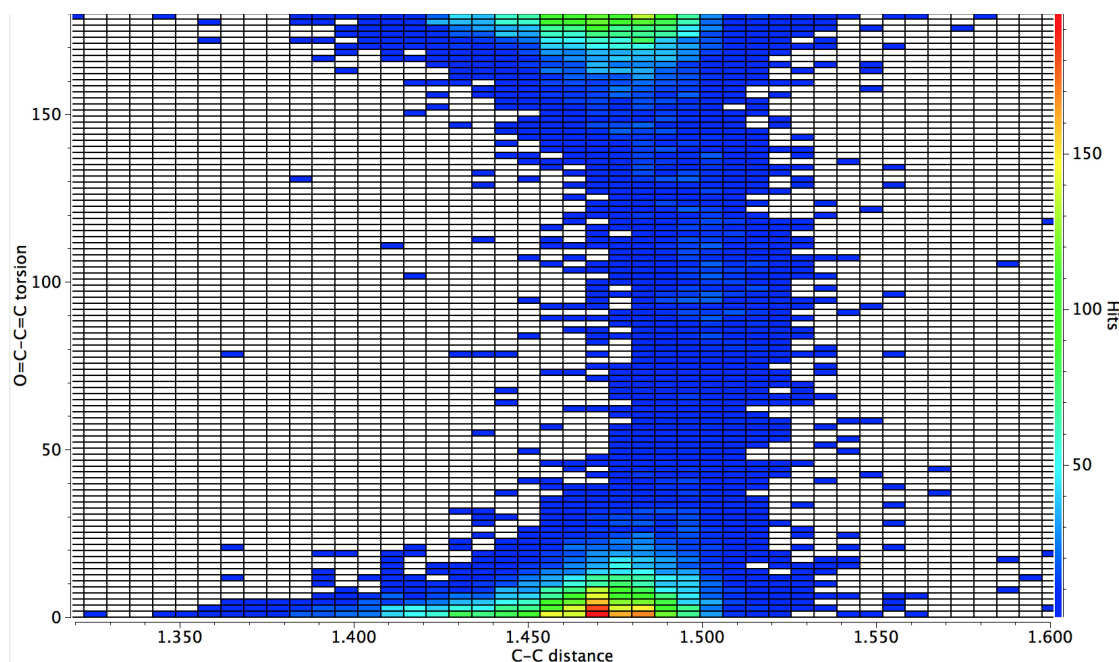
1. Note first that the hotspot occurs for a torsion angle of 180° , a trans diene.
2. There is just a hint that the C-C distance for a cis-diene might be a little shorter than the trans diene, but this might not be significant.
3. There is a gentle curve illustrating that the C-C distance is indeed a maximum at 90°
4. The C-C bond extends from $\sim 1.445\text{\AA}$ when the two double bonds are coplanar (fully conjugated) to $\sim 1.48\text{\AA}$ when orthogonal. Not much of a change, but statistically highly significant.

Here is another search, this time of the $\text{C}=\text{C}-\text{C}=\text{C}$ motif embedded into a biaryl, of which there are far more examples. This time, the (red) hotspot is actually at 90° , with local (green) hotspots at 0 and 180° but also at 45° and 135° . Again, you can easily spot the maximum in C-C bond length at 90° but notice how much smaller the bond lengthening is ($\sim 0.01\text{\AA}$). This lengthening is inhibited by retention of the aromaticity of the two aryl rings; again the statistical effect is highly significant. Perhaps also significant is that the C-C bond at torsions of 0 or 180° appear to be no shorter than the values at 45° and 135° .

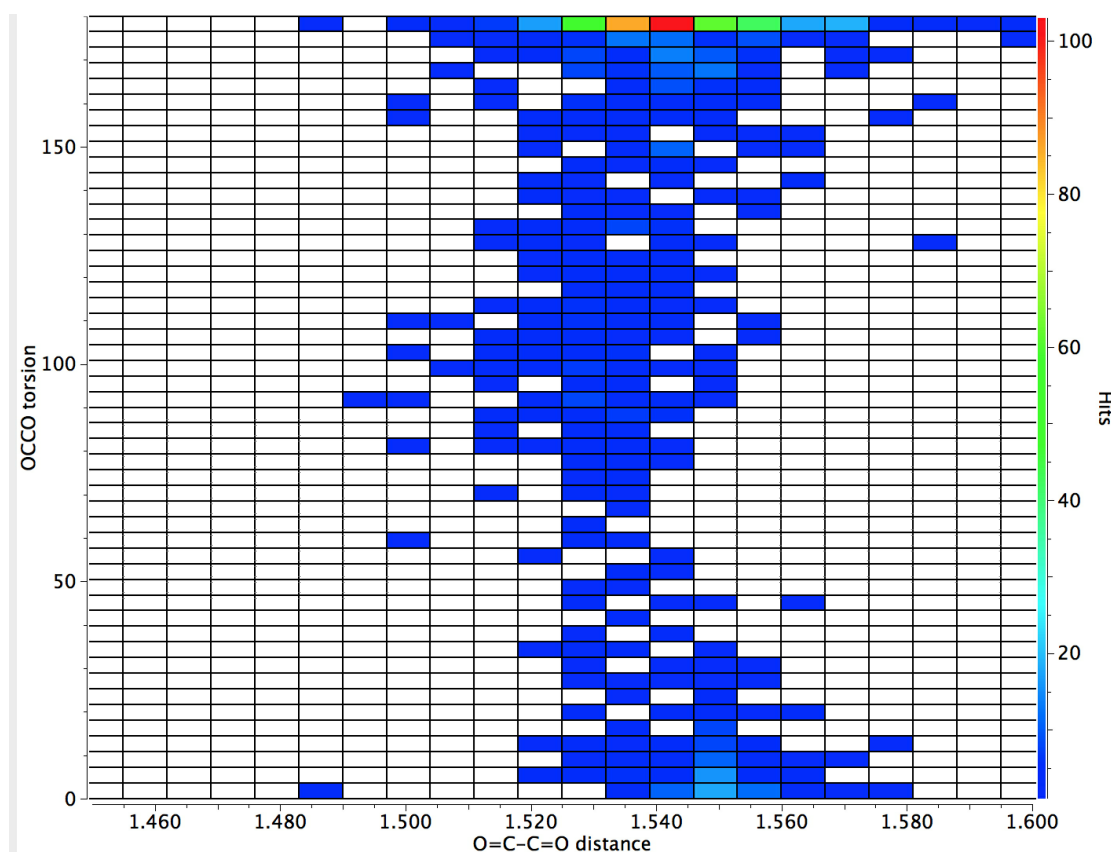


Both these searches took about 5 minutes each, and serve to illustrate just how many basic chemical concepts can be teased out of a statistical analysis of crystal structures.

‡ The analogous diagram for O=C-C=C is shown below;



That for O=C-C=O is different however;



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