π-Resonance in thioamides: a crystallographic “diff” with amides.

Henry Rzepa[1]

[1]Affiliation not available

April 17, 2023

the
WINNOWER

CHEMISTRY

π-Resonance in thioamides: a crystallographic "diff" with amides.

HENRY RZEPA

READ REVIEWS

WRITE A REVIEW

CORRESPONDENCE:
h.rzepa@imperial.ac.uk

DATE RECEIVED:
September 13, 2015

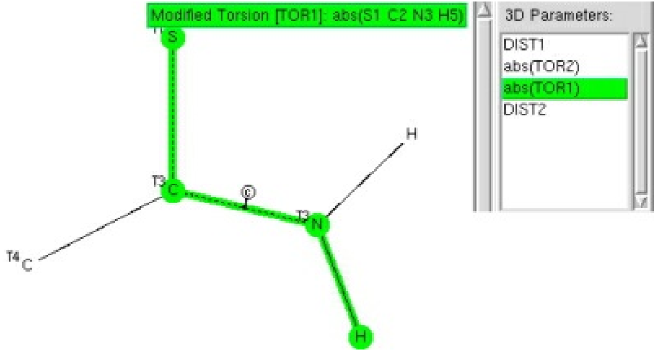
DOI:
10.15200/winn.144212.25425

ARCHIVED:
September 13, 2015

CITATION:
Henry Rzepa, π-Resonance in thioamides: a crystallographic "diff" with amides., *The Winnower* 2:e144212.25425 , 2015 , DOI: 10.15200/winn.144212.25425

0000-0002-8635-8390

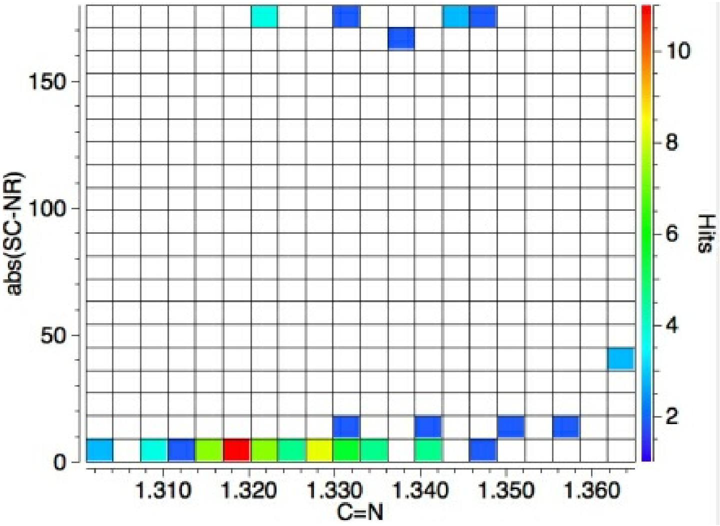
The previous post explored the structural features of amides. Here I compare the analysis with that for the closely related thioamides.



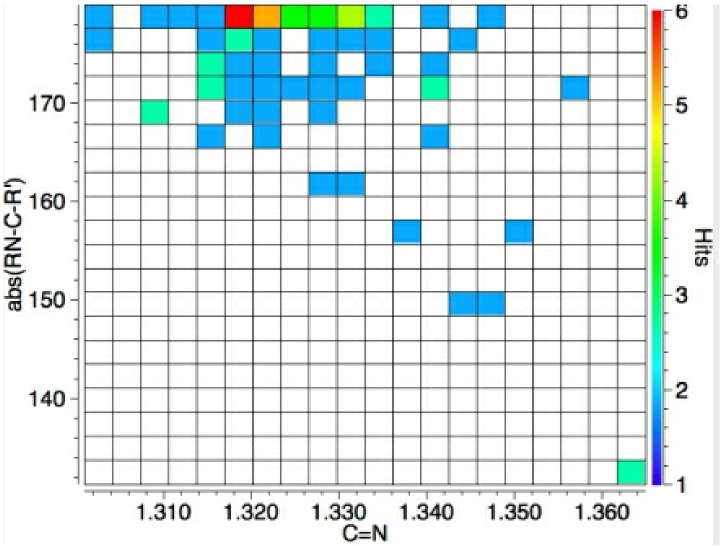
Modified Torsion [TOR1]: abs(S1 C2 N3 H5)

3D Parameters:
DIST1
abs(TOR2)
abs(TOR1)
DIST2

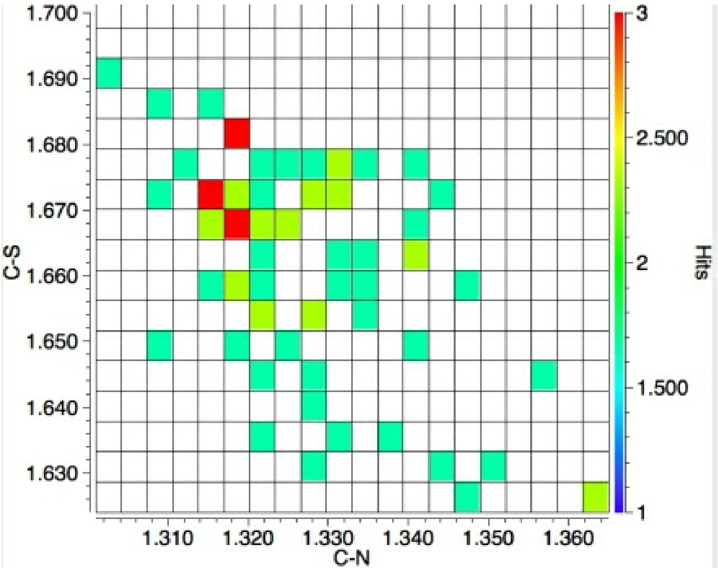
Here is the torsional analysis around the C-N bond. The "diff" (difference) is that almost all the hits are concentrated into angles of 0° or 180°; the twist about the C-N bond from co-planarity is much less if S is present. This is normally explained in terms of Spπ-Cpπ overlaps being less favourable than Opπ-Cpπ ones owing to the mismatch in the size of the atomic orbital for S and C. Hence the resonance which reduces the C=S double bond character in favour of greater C=N character is enhanced compared to O.



A consequence is that the nitrogen atom is less easily deformed from planarity in a thioamide. Notice also that at the hotspot, the C=N distance is ~1.32Å compared to 1.34Å for a regular amide.



This emerges from the plot below as well; the range of values for the C-N bond is reduced compared to amides, but the diagonal trend that as the C=N bond gets longer so the C-S gets shorter is still seen.



All these trends are described qualitatively in most text books of organic chemistry, but one never sees statistical evidence for them. And it truly only takes 5-10 minutes to produce.