

Gauging the strength of donor acceptor interactions in organic molecules

Jonathan White¹, Brett Pool¹, Benjamin Harris¹, Shinn-Dee Yeoh¹

¹*School Of Chemistry And BIO-21 Institute, University Of Melbourne, Melbourne, Australia*

E-mail: whitejm@unimelb.edu.au

The variable oxygen probe is an x-ray crystallographic method for measuring the strength of the interaction between a donor orbital and an acceptor orbital in being the antibonding orbital of an oxygen substituent.¹ When the electron demand of the oxygen substituent is increased then the C-OR bond lengthens due to increased contributions of the no-bond resonance form (C-OR, C+ OR-), the sensitivity of the C-OR bond distance to the electron demand of the OR group is related to the strength of donor orbitals which are suitable oriented to donate electron density into the C-OR σ^* orbital.

Application of the variable oxygen probe to a range of suitable organic compounds has not only provided information on the relative donor abilities of a variety of functional groups, but also allows us to uncover the effects of strain on donor ability. Perturbations in the remainder of the structure can often provide clues on the mechanism of electron transfer from the donor to the varying oxygen acceptor, and can provide a picture of the early stages of a molecular rearrangement.

1 Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. J. *Am. Chem. Soc.* 1984, 106, 6200,

2 White, Amos, R. D.; Handy, N. C.; Jones, P. G.; Kirby, A. J.; Parker, J. K.; Percy, J. M.; Der Su, M. J. *Chem. Soc. Perk. Trans.* 2 1992, 549.

3 J. M. White In *Topics in Stereochemistry*; Denmark, S., Ed.; John Wiley and Sons

Keywords: [hyperconjugation](#), [strain](#), [rearrangement](#)