

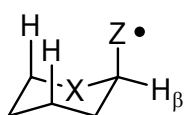
# Radicals Attached to 6-Membered Rings. An Experimental and Theoretical Study of Axial and Equatorial Orientations

John C. Walton,<sup>a</sup> Mark D. Roydhouse<sup>a</sup> and Gino A. DiLabio<sup>b</sup>

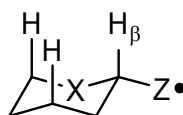
<sup>a</sup> University of St. Andrews, School of Chemistry, St. Andrews, Fife KY16 9ST

<sup>b</sup> National Research Council of Canada, W6-010 ECERF, 9107 116th Street, Edmonton, AB, Canada T6G 2VA

The reactivities of cyclic transient radicals depend on whether the unpaired electron is sited on a group Z that is axial **A** or equatorial **E** to the ring.



**A**  
Z = CH<sub>2</sub>, C=O, O-O,  
X = CH<sub>2</sub>, O



**E**  
Z = CH<sub>2</sub>, C=O, O-O,  
X = CH<sub>2</sub>, O

For cyclohexylmethyl (Z = CH<sub>2</sub>) and many other cycloalkyl- and heterocycloalkyl-methyl radicals the two species have distinct isotropic EPR spectra in solution that enable conformation-dependent processes to be monitored.<sup>1</sup> Steric repulsion between syn-axial hydrogen atoms and the axial radical centre Z<sup>•</sup> leads to a significantly increased internal rotation barrier about the C<sub>β</sub>-Z bond in axial radicals. As a consequence axial and quasi-axial radicals have much greater H<sub>β</sub> hyperfine splittings than equatorial radicals.

The main EPR spectrum obtained on hydrogen abstraction from cyclohexane carbaldehyde had a triplet structure at low temperatures and a *g*-factor consistent with the **E**-conformer of the cyclohexylacyl radical (**E**, Z = C=O). The wings of this spectrum showed additional weak features. Comparison of the spectrum with that of the axial 4-*t*-butylcyclohexylacyl radical derived from *trans*-4-*t*-butylcyclohexane carbaldehyde showed that these wings were due to the axial conformer (**A**, Z = C=O).<sup>2</sup>

DFT computations (B3LYP/6-31-G\*) were carried out on the axial and equatorial cyclohexylacyl radicals and axial and equatorial cyclohexylmethyl radicals to predict their relative energies. The rotational potentials about the C<sub>β</sub>-Z bonds were also computed and these enabled the unexpected triplet fine structure of **E**(Z = C=O) to be explained.

EPR spectra for analogous tetrahydropyranacyls and for cyclohexylperoxyl radicals will also be reported.

1. K. U. Ingold and J. C. Walton, *Acc. Chem. Res.* 1989, **22**, 8.
2. G. A. DiLabio, K. U. Ingold, M. D. Roydhouse and J. C. Walton, *Org. Lett.* 2004, **6**, 4319.