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MAGNETIC SHIELDING OF ALPHA PROTONS BY THE CARBONYL GROUP IN CYCLOHEXANONES

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The original observation that axial protons in cyclohexane and pyran systems absorb at higher p.m.r. fields than their equatorial counterparts[1a] has been followed by numerous similar reports, and has been stated in the form of a general rule.[1b] In contrast, Williamson and Johnson noted that the axial 3α proton in 3β-acetoxy-5α-cholestan-2-one resonates at a lower field than the comparable 3β equatorial proton in its 3α-acetoxy epimer.[2] We wish to report a number of other instances where axial protons alpha to the carbonyl group in cyclohexanones absorb at lower field than their equatorial counterparts (Table I).

1(a) R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, J. Am. Chem. Soc., 80, 6098 (1958);

(b) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry", Pergamon Press, 1959, p. 116.

2 K. L. Williamson and W. S. Johnson, J. Am. Chem. Soc., 83, 4623 (1961).

TABLE I[a]

Chemical Shifts of -CHBr Protons in Some

α-Bromocyclohexanones

4-Phenylcyclohexanone	Configuration of -CHBr Proton	Chemical Shift (p.p.m.)
cis-2-Bromo-	axial	4.87
trans-2-Bromo-	equatorial	4.38[c]
cis,*cis*-2,6-Dibromo-	axial	4.90
cis,*trans*-2,6-Dibromo-	equatorial[b]	4.62
4-*t*-Butylcyclohexanone		
cis-2-Bromo-	axial	4.67
trans-2-Bromo-	equatorial	4.29
cis,*cis*-2,6-Dibromo-	axial	4.78
cis,*trans*-2,6-Dibromo-	equatorial[b]	4.58

[a] The spectra were recorded on a Varian High-resolution spectrometer operating at 60 mc. The position of the signals relative to tetramethylsilane ($\delta = 0$) was determined by extrapolation between audiofrequency side bands and was reproducible to ±0.03 p.p.m.. Measurements were made on chloroform solutions (ca. 12% W/W) except for the *cis*- and *trans*-2-bromo-4-*t*-butylcyclohexanones which were determined in carbon tetrachloride.

[b] Of the two -CHBr protons, only the chemical shift of the equatorial proton is reported.

[c] This chemical shift was kindly furnished by Dr. E. W. Garbisch, Jr.

Inspection of the chemical shifts in each of the two pairs of monobromo- and dibromocyclohexanones shows that in every instance the axial -CHBr proton appears at lower field than the corresponding equatorial proton. Since the bromine atom is axially symmetric, these observations remove the possibility that the order of absorptions noted by Williamson and

Johnson[2] is due to an effect exerted by a preferred conformation of the acetoxy group. Nor is it likely that this unexpected relative order of chemical shifts is caused by polar effects of the solvent or by bond anisotropies. The same effect has now been observed in a variety of solvents, including carbon disulfide,[2] carbon tetrachloride, chloroform, and acetonitrile.[3,4] Carbon-carbon bond anisotropies should produce an effect opposite to that observed, according to the information available from cyclohexane systems.[1b] The rough mapping of the magnetic anisotropic effects of the carbonyl group also leads to an opposite prediction.[5] The relative chemical shifts of the protons in question appear to be best correlated with the direction of the carbonyl bond dipole and its resultant electrostatic field. The dipole moments of *cis*- and *trans*-2-bromo-4-*t*-butylcyclohexanones have been reported to be 4.27 D and 3.20 D, respectively,[6] and will be oriented approximately as shown in I and II. It has been

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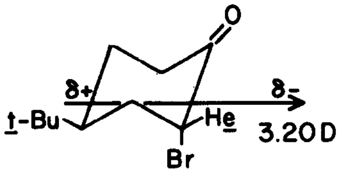
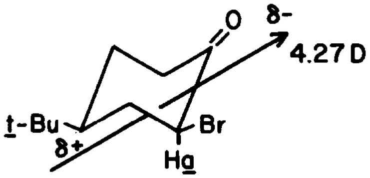
[3] N. L. Allinger, M. A. DaRooge, M. A. Miller, and B. Waegell, *J. Org. Chem.*, **28**, 780 (1963), have observed that the -CHF axial proton in 2α-fluoroandrostan-3,17-dione appears downfield as compared to the equatorial proton in the 2β-fluoro epimer in either deuterochloroform or acetonitrile. Professor Allinger has informed us that the chemical shifts in his Table II are on the tau scale, and that the value reported as 3.92τ should be 4.92τ.

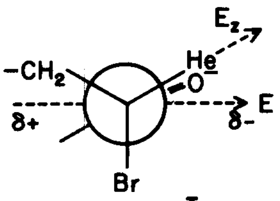
[4] Unpublished results of E. W. Garbisch, Jr., University of Chicago, have shown that the chemical shifts of the axial and equatorial protons converge on dilution, but do not reverse. We wish to thank Dr. Garbisch for several helpful discussions.

[5] See Ref. 1b, p. 124. See also O. L. Chapman, H. G. Smith, and R. W. King, *J. Am. Chem. Soc.*, **85**, 806 (1963).

[6] N. L. Allinger, J. Allinger and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 2926 (1960).







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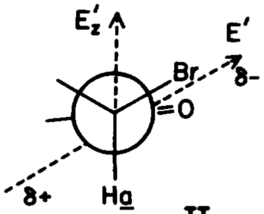

II

demonstrated in a number of instances that the shielding at a nucleus varies according to local electric fields experienced by the nucleus as produced by electrostatic fields set up by solvent molecules^{7,8,9} or by polar groups within the solute molecule itself.$^{8\ 10-12}$ In I, the component (E_z) of the electric field (E) oriented along the C-H bond increases the electron density at the equatorial proton, producing a diamagnetic shift, whereas in II the comparable component is directed away from the proton and withdraws electrons, causing a downfield shift of the signal for the axial proton. It is

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[7] A. D. Buckingham, T. Shaeffer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[8] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

[9] P. Diehl and R. Freeman, *Mol. Phys.*, **4**, 39 (1961).

[10] J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

[11] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

[12] G. S. Reddy, C. E. Boozer, and J. H. Goldstein, *J. Chem. Phys.*, **34**, 700 (1961).

of interest to note that the chemical shift of the equatorial C-1 proton in *cis*-4-*t*-butylcyclohexyl bromide is 4.6 p.p.m., whereas that for the axial C-1 proton in the trans isomer is 3.80 p.p.m.[13] Comparison of these values with those in Table I shows that the introduction of the carbonyl group into the cyclohexane nucleus causes a slight shielding of the equatorial -CHBr proton (δ =4.4 p.p.m.) and a large deshielding of the axial -CHBr proton (δ = 4.8 p.p.m.), in qualitative agreement with the effect expected on the basis of dipole moment considerations.

In view of the well documented interaction established for the sigma bond of axial protons and the pi bond of an adjacent carbonyl group in the enolization of cyclohexanones[14], it seems likely that a similar effect may operate in the ground state, and that an overlap of this type[15,16] may also be promoting a downfield shift for the axial proton relative to the equatorial proton.

If the relative deshielding of the axial protons in cyclohexanones is indeed caused primarily by the carbonyl

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[13] E. L. Eliel, *Chem. Ind.*, 568 (1959).

[14] E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **78**, 6269 (1956), and earlier papers.

[15] R. A. Beaudet and J. D. Baldeschweilder, *J. Mol. Spect.*, **9**, 30 (1962).

[16] R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.*, 806 (1963).

Added note: After this manuscript had been submitted, a communication appeared [A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *J. Am. Chem. Soc.* **85**, 2185 (1963)] which reported similar results for the α-protons in a variety of α-halo steroids.

dipole, augmented by σ,π-bond overlap, the signal for an axial proton alpha to the carbonyl group in a cyclohexanone can be expected to appear in p.m.r. spectra at a downfield position relative to its equatorial counter part.

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