Tetrahedron Letters No. 20, pp 1733 - 1734, 1976. Pergamon Press. Printed in Great Britain.

HIGH RESOLUTION DEUTERIUM MAGNETIC RESONANCE OF UNSYMMETRICALLY SUBSTITUTED PROPANES.[1]

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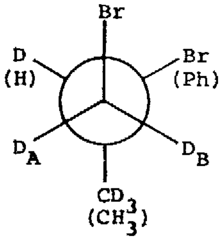
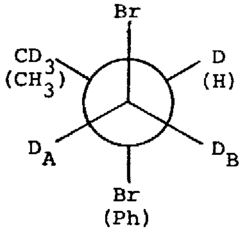
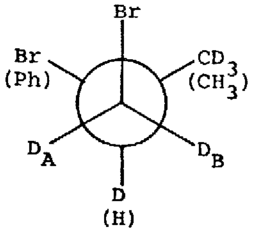
(Received in UK 23 March 1976, accepted for publication 5 April 1976)

The ^2H nmr spectra of a number of selectively deuterated bromopropanes are shown in the Figure In contrast to ^1H nmr spectra,where usually a spectral analysis has to be performed to evaluate the chemical shift of individual protons,^2H nmr allows the corresponding deuterium chemical shift (which compares closely with the corresponding proton shift) to be measured directly from the spectrum.The assignment of the individual deuterium resonances in perdeuterio-1,2-dibromopropane (I) is straightforward,as seen by inspection of the ^2H nmr spectra of the partially deuterated 1,2-dibromopropanes II and III in the Figure

Of particular interest are the resonances of the two deuterons in the CD_2 group of I and IV,which is attached to an optically active carbon atom Such an asymmetric carbon can induce chemical shift nonequivalence.In the present case even with rapid interconversion between,and equal populations of the three classical conformers represented below,chemical shift nonequivalence of the two methylene deuterons,D_A and D_B,is made evident by ^2H nmr In both cases the CD_2 group shows two peaks of equal intensity,the chemical shift difference being 0.34 ppm and 0.26 ppm for I and IV,respectivelly.

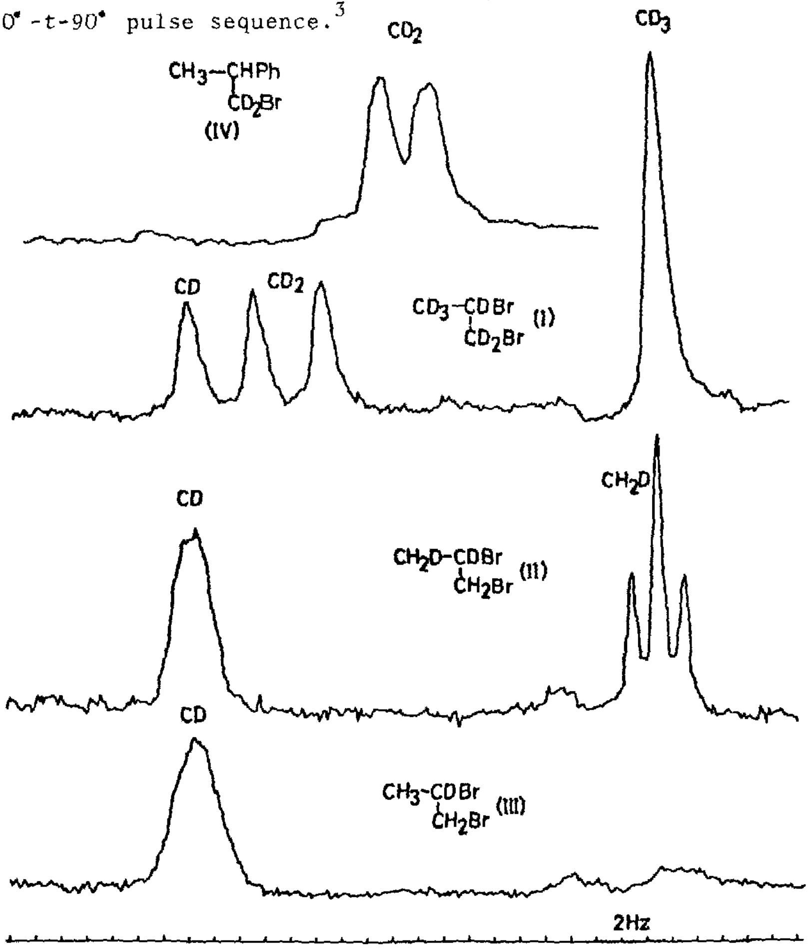






It is interesting to note that the T_1 values of the CD_2 deuterons in IV (0.34 sec.) are considerably shorter than those of I (0.58 sec) Since the spin-lattice relaxation times of the individual deuterons of acyclic compounds become shorter when the internal rotation is hindered by substitution of chlorine or bromine[2],it may be concluded that the potential barrier of internal rotation in IV is higher than that of I

FIGURE. Fourier transformed ^2H nmr spectra (15.4 MHz,Varian XL-100-15) of *selectively deuterated 1,2-disubstituted propanes as 5% solutions in CCl_4 in* 12 mm tubes with TMS concentrics for field frequency stabilization.Deuterium spin-lattice relaxation times were measured by the inversion recovery method using a 180°-t-90° pulse sequence.[3]



The high resolution ^2H nmr spectra of I and IV demonstrate the magnetic nonequivalence *phenomenon*,as well as the sensitivity of the deuterium chemical shift and relaxation times,to substitution on the neighboring carbon atom.

REFERENCES AND NOTES

1. The experimental part was completed at the Division of Biological Sciences National Research Council of *Canada*,*Ottawa*.The *authors are grateful to Dr Ian C.* P.Smith for discussions and to Dr.L.C.Leitch *for* a gift of deuterated compounds.

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