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STEREOSPECIFIC LONG RANGE COUPLINGS IN THE NMR SPECTRA OF SUBSTITUTED 1,3-DIOXANES

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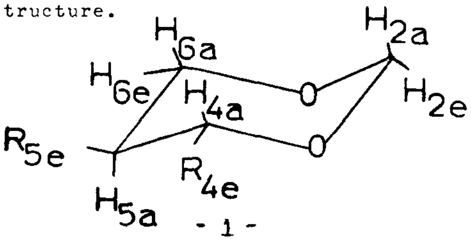
The use of stereospecific long range couplings in the elucidation of complex molecular structures is of considerable importance and has been the subject of a number of recent reports (1-3). The interaction of protons separated by four single bonds is of particular interest in the study of saturated cyclic systems. However, the paucity of data on simple molecules containing protons which conform to a near planar zigzag configuration seriously limits significant correlations of $^{4}J_{HH}$ with respect to bond angles and substituents.

Recent reports(4-7) on the n.m.r. parameters of substituted 1,3-dioxanes clearly show that the 4 and 4,5 substituted compounds exist in the chair conformation with the substituents equatorially disposed as depicted in the following structure.



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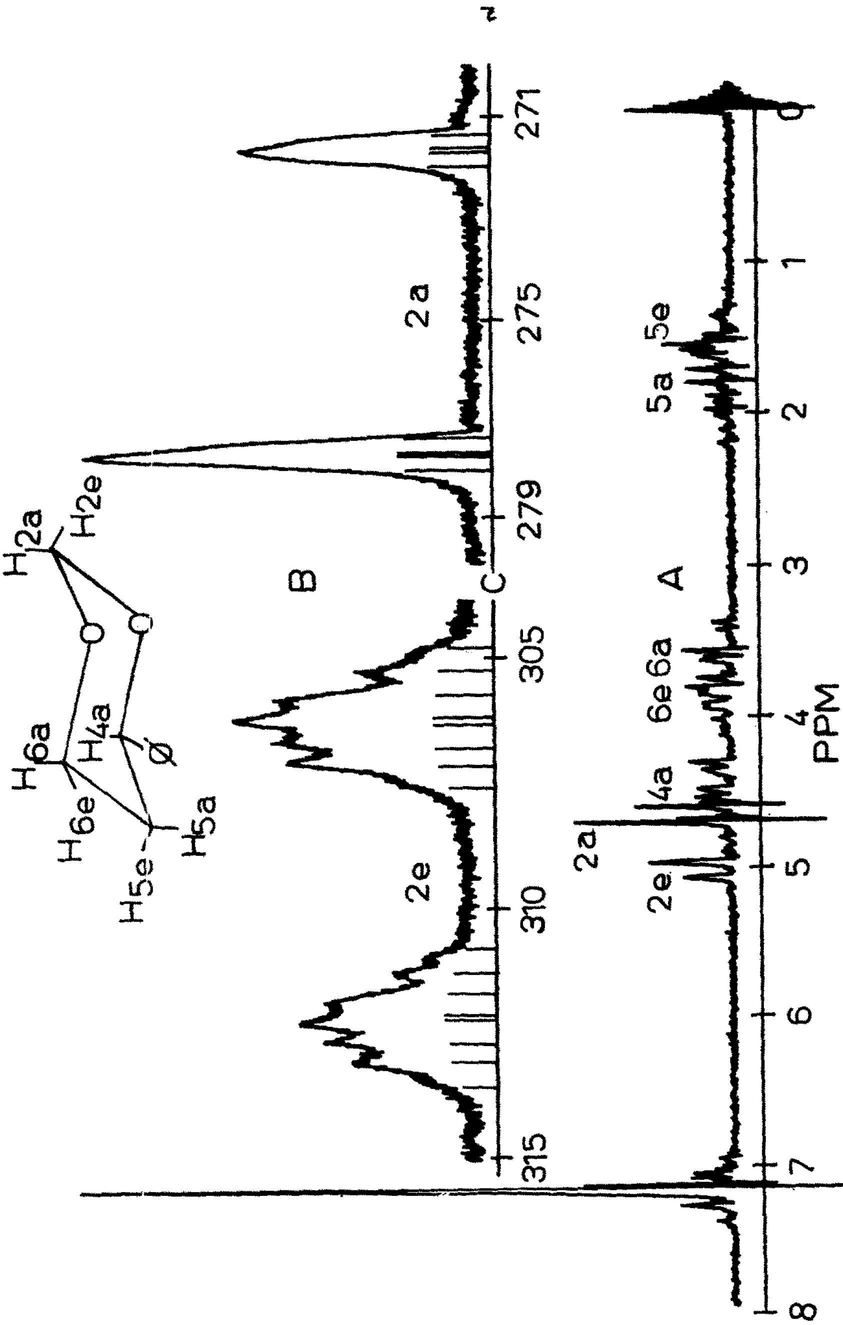

FIG. 1. A, NMR spectrum of 4-phenyl-1,3-dioxane, B, a slow sweep of the resonances for protons **2a** and **2e**, and C, calculated resonances in c.p.s. from TMS for protons **2e** and **2a** based on the parameters in Table 1.

The 60 Mc./sec., n.m.r. spectrum of 4-phenyl-1,3-dioxane and a slow sweep of the resonances for protons 2a and 2e are depicted in Fig. 1. The calculated spectrum(8) is in good agreement with the observed spectrum and the AB portion corresponding to 2a and 2e is depicted in Fig. 1. The interaction of 2e with 6e was expected since they conform to a planar zigzag arrangement(1-3). However, the additional couplings of 0.9 and 0.5 c.p.s. were not expected on the basis of systems thus far studied(2). A slow sweep of the normal resonance(100 Mc./sec.) of 5e is depicted in Fig. 2A, which not only shows the geminal and vicinal couplings, but an additional coupling of 0.9 c.p.s. The resonance of 5e decoupled(9) from 2e is depicted in Fig. 2B, and clearly shows that $\left|J_{2e5e}\right| = 0.9$ c.p.s. This appears to be the first case of an interaction across five single bonds within a rigid system.

The various coupling constants for 4-phenyl-1,3-dioxane were elucidated by the double resonance technique and are depicted in Table 1. A number of long range couplings of 0.5 cps. or less were indicated by the spectra and some of these are listed below.

FIG. 2

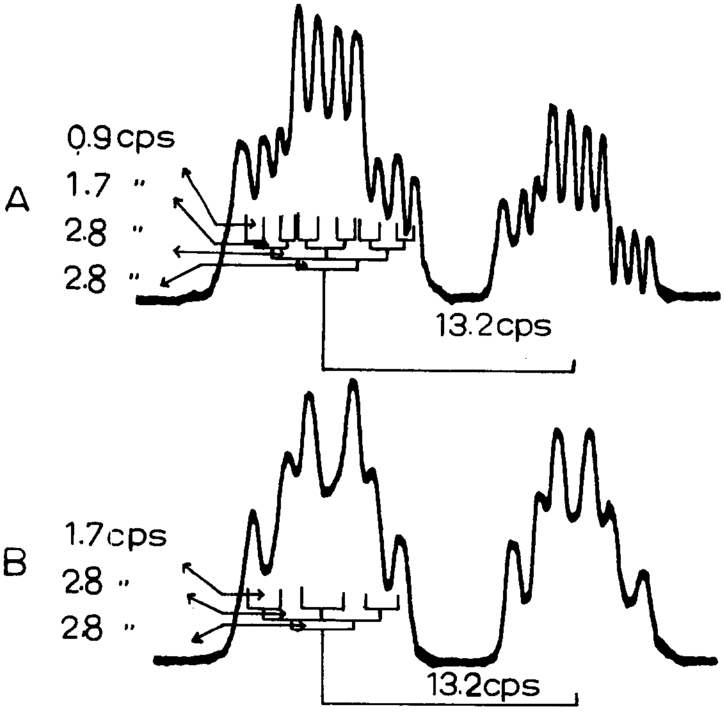

FIG. 2. NMR spectra, A, normal resonance for proton 5e, and B, the resonance of 5e decoupled from 2e ($\Delta\nu$ = 3.39 ppm).

TABLE I

Coupling Constants for 4-phenyl-1,3-dioxane(c.p.s.)

Geminal	Vicinal	Long Range
$J_{2e2a} = -6.2^{a}$	$J_{4a5a} = +11.0$	$\lvert J_{2e6e} \rvert = 1.5$
$J_{5e5a} = -13.2$	$J_{4a5e} = +2.8$	$\lvert J_{2e5e} \rvert = 0.9$
$J_{6e6a} = -11.2$	$J_{5a6e} = +5.0$	(tentative assignment)
	$J_{5a6a} = +11.0$	$\lvert J_{2e6a} \rvert = 0.5$
	$J_{5e6e} = +1.7$	$\lvert J_{6e4a} \rvert = 0.5$
	$J_{5e6a} = +2.8$	$\lvert J_{6e2a} \rvert = 0.4$
		$\lvert J_{6a4a} \rvert = 0.4$
		$\lvert J_{6a2a} \rvert = 0.3$

a- assumed negative, J. A. Pople and A. A. Bothner-By, J. Chem. Phys., 42, 1339 (1965).

The spectrum of 4-methyl-1,3-dioxane yielded similar long range couplings of 0.7 and 1.5 c.p.s. for $\lvert J_{2e5e} \rvert$ and $\lvert J_{2e6e} \rvert$, respectively.

These results indicate that considerable caution should be used in assigning long range interactions, since a planar zigzag arrangement is not necessary for couplings of the order of 0.5 c.p.s. Furthermore, couplings of the order of 1.0 c.p.s. between protons separated by five single bonds must be considered.

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8. The authors would like to thank Dr. A. A. Bothner-By of Mellon Institute for a copy of his IBM 704 program.

9. Decoupling was carried out with a Varian Integrator utilizing the field sweep technique, L. F. Johnson, Varian Associates Technical Information Bulletin, III, No. 3, 5 (1962).