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NMR STUDIES OF RIGID BICYCLIC SYSTEMS. III.[1] ASSIGNMENT OF CHEMICAL SHIFT VALUES IN THE NMR SPECTRUM OF NORBORNANE

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Nmr chemical shift correlations involving the exo and endo protons in 5- and 6- substituted norborn-2-enes have proved useful in making configurational assignments in these systems.[2] Many of these assignments can be confirmed through the observation of stereospecific long-range couplings.[3] However, neither of these techniques has proved generally useful in norbornane and related systems, as their nmr spectra are usually more complex and the individual features are more obscured than in the corresponding norbornenes.[4]

Nevertheless, some chemical shift correlations in norbornanes have been made. In a study involving a number of bicyclo(2.2.1)heptanols, Musher[5] found that exo protons are deshielded relative to endo protons by ca. 0.3-0.5 ppm; this same observation has been noted in a more recent study involving 7-substituted 1,4-dichloronorbornanes.[1] Musher[5] has suggested that the observed magnetic nonequivalence between exo and endo protons reflects magnetic anisotropy features inherent in the bicyclo(2.2.1) heptane ring system itself.

Previously, detailed study of the nmr spectrum of the parent norbornane has been precluded by its overriding complexity. We have approached this problem through synthesis and examination of the nmr spectra of a number of specifically deuterated norbornanes; the nmr spectra of eight of these (plus the parent compound) are shown in the accompanying figure. Isotopic analyses, determined mass spectrometrically, are indicated in each of the insets, B through I. Syntheses of the deuterated norbornanes were effected by reduction of the corresponding chloronorbornanes[6] with Na-tBuOD[7] or from the corresponding chloronorbornenes[3] utilizing D_2 over palladized charcoal followed by Na-tBuOD reduction of the resulting deuteriochloronorbornanes.[3,7]

Comparison of the nmr spectrum of norbornane (inset A) with that of exo, exo,exo,exo,-2,3,5,6-tetradeuterionorbornane (inset D) and with that of 7-deuterionorbornane (inset F) reveals that the endo protons absorb at δ 1.13, essentially coincident with the bridge (7-) protons; (the singlet at δ 1.13 in inset D has width at half-height = W_H = 2.5 Hz). Insets C and E, respectively, reveal the

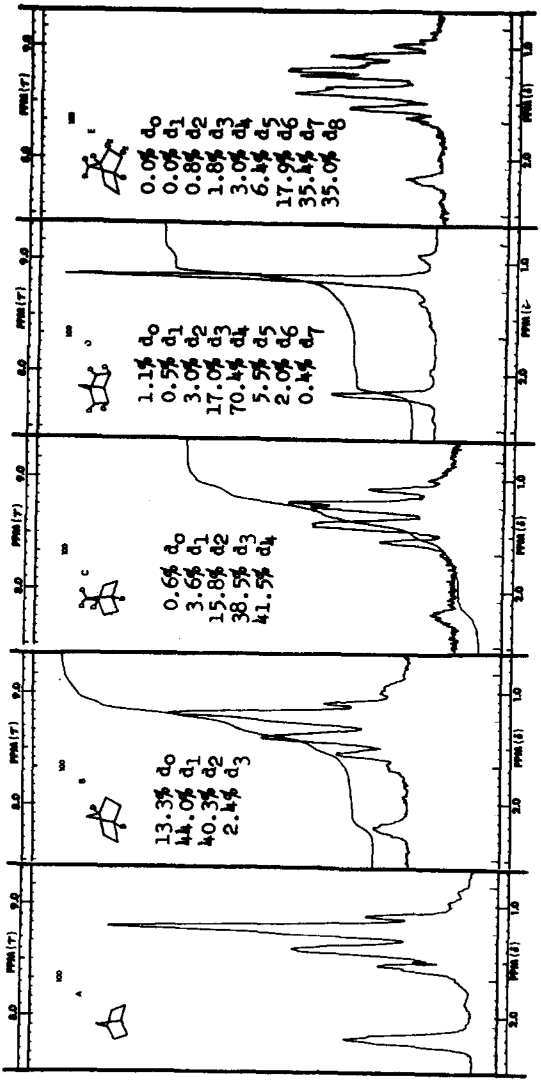

Figure 1. 60 MHz NMR Spectra (TMS Internal Standard, CCl_4 Solution) and Isotopic Analyses of Deuterionorbornanes.

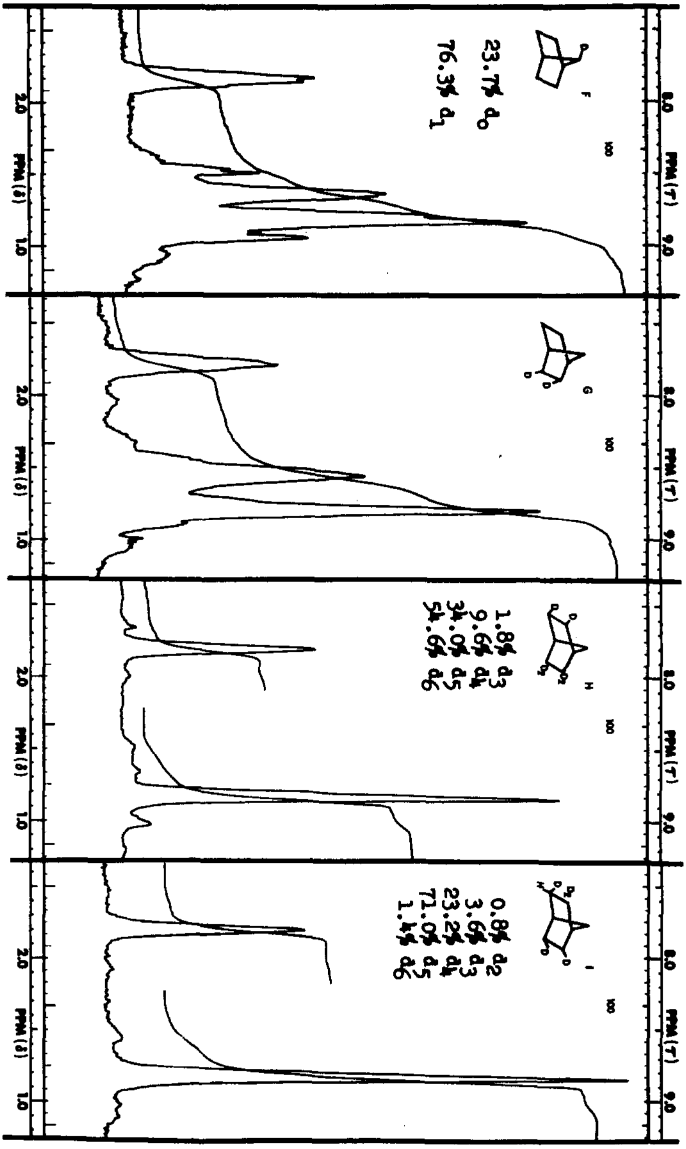

Figure 1, continued.

AA'A"A'"B'B"B"' and AA'BB' norbornane exo,endo proton patterns.

The table below indicates the chemical shifts in ppm and the difference, Δδ, between the exo and endo protons in norbornane and in norbornene[3]:

Compound	δ endo	δ exo	Δδ (Hz)
Norbornane[a]	1.13	1.43	0.30
Norbornene[b]	0.96	1.59	0.63

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[a] Calculated from the AA'BB' nmr spectrum of 1,2,2,3,3,4,7,7-octadeuterionorbornane, (inset E.). Reference 10.

[b] Reference 3.

Significantly, these results confirm Musher's previous conclusions[5] by suggesting that the chemical shift difference Δδ in norbornene is primarily a feature of this strained ring system. The anisotropy of the 2,3-double bond is apparently not the major cause of the often observed exo, endo chemical shift difference in substituted norbornenes.[8] This conclusion underscores the unreliability of configurational assignments which are based solely on anticipated anisotropy effects of the norbornene double bond. Other supporting evidence (e.g., observation of stereospecific long-range couplings) is desirable when such assignments are to be made utilizing nmr spectroscopy.

Our ultimate objective is to calculate the various nmr spectral parameters of the parent norbornane utilizing the LAOCOON III computer program[9] and the deuterated norbornanes shown in the accompanying figure. We plan to report the results of these calculations shortly.[10]

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