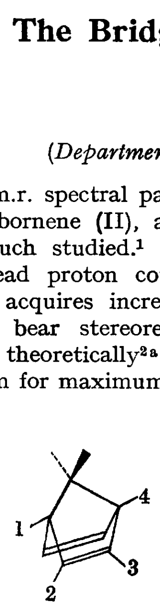
The Bridgehead Proton Spin Couplings in Norbornene and Norbornadiene

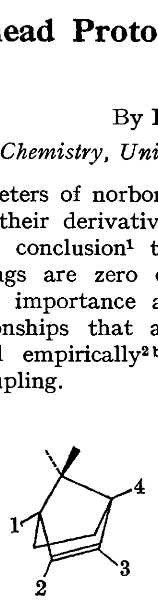
By EDGAR W. GARBISCH, JUN.

(*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota* 55455)

THE n.m.r. spectral parameters of norbornadiene (I), norbornene (II), and their derivatives have been much studied.[1] The conclusion[1] that the bridgehead proton couplings are zero or close thereto acquires increased importance as these protons bear stereorelationships that are considered theoretically[2a] and empirically[2b] to be optimum for maximum coupling.



(I)



(II)

If the only nonzero couplings involving the vinyl protons are retained in the labelled fragments of (I) and (II), their n.m.r. spectra may be analyzed as arising from the AA' parts of $AA'XX'$ systems, the XX' parts being the bridgehead protons. Second-order corrections are all less than 0·03 c./sec. The analyses give $J_{1,4}$, $J_{2,3}$, $J_{1,2}$, and $J_{1,3}$, the relative signs of the latter two couplings being determined. However, $J_{1,4}$ cannot be distinguished from $J_{2,3}$ nor can $J_{1,2}$ be distinguished from $J_{1,3}$.[3] Analysis of the ^{13}C–H satellite resonances of the vinyl protons provides a means for characterization of the former pair of couplings; the latter pair being characterized *a priori*.

In 1959 Mortimer reported the analysis of the n.m.r. spectrum of (I).[1a] The parameter $J_{1,4}$, the cross-ring vinyl–vinyl and the vinyl–methylene proton couplings were explicitly taken as being zero in deriving expressions for the state eigenvalues.

If $J_{1,4}$ is nonzero, four additional transitions may become observable, two being of low intensity at the extremities of the spectrum and two being of high intensity at the innermost part of the spectrum.

The cross-ring vinyl–vinyl proton couplings in derivatives of (I) have been found[1b] to be negligible, however the vinyl–methylene proton couplings may not be so.[1b] The 60 Mc./sec. frequency-swept n.m.d.r. spectrum[†] of the vinyl protons of (I) with H-2 = 0·5 mG at the methylene proton frequency is shown in Figure 1A. There was no significant narrowing of the vinyl proton resonances in the double resonance spectrum as compared with the normal one, the band widths at half height ($W_{\frac{1}{2}}$) being *ca.* 0·3 c./sec. in both. The vinyl–methylene proton coupling therefore must be negligible. However, there are two too many transitions at the extremities of the spectrum. The transitions b and b' saturate more readily than their neighbouring ones (a, c and a' c') as seen from the spectra shown in Figure 1B and 1C (recorded at H-1 fields of 0·005 and 0·1 mG, respectively). For a given spin system, states connecting transitions of low intensity should become less saturated than those connecting transitions of higher intensity upon increasing H-1. Consequently, it appears reasonable to conclude that transitions b, and b' are not part of the H^{12}C–^{12}CH spectrum. Further, analysis of the spectrum retaining b and b' and neglecting a and a' or c and c' gives parameters that are in substantial disagreement with the ^{13}C–H satellite analysis parameters (see Table).

[†] All spectra were determined on an A60 spectrometer with a V6058A decoupler, both modified to allow frequency sweep of the 5 Kc./sec. field modulation over 4·5—5·5 Kc/sec.

Normal 60 Mc./sec. vinyl proton spectra of (II) are shown in Figure 2A and 2B. The resonances of the six bridge protons appear as a complex band between ν_{TMS} +45 and +110 c./sec.‡ The $W_{\frac{1}{2}}$ of the vinyl proton resonances decreased from 1·3 in the normal spectrum to 0·5 c./sec. in the frequency-swept n.m.d.r. spectrum where an H-2 ~ 4 mG was set at ν_{TMS} +63 c./sec. The weak transitions at the extremities of the spectrum are shown in Figure 2C. Transitions having $W_{\frac{1}{2}}$ = 0·35 c./sec. were obtained by placing an H-2 of 3 mG at ν_{TMS} +66·5 and modulating the field with a frequency of 8·8 c./sec. to give H-2 = 2 mG (ν_{TMS} + 66·5 c./sec.) H-3 = 0·5 mG (ν_{TMS} + 58·0 c./sec.), and H-4 = 0·5 mG (ν_{TMS} + 75·6 c./sec.). The resulting frequency-swept vinyl-proton spectrum is shown in Figure 2D (H-1 modulation sidebands interfere with the recording of the low intensity transitions). The results of the analysis of the spectra shown in Figures 2C and 2D are given in the Table.

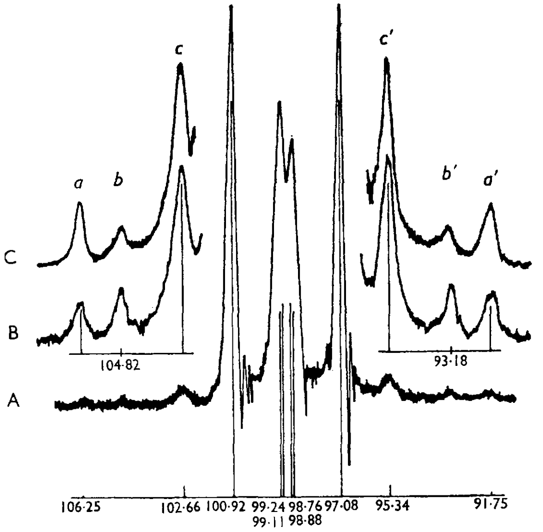


FIGURE 1. *Frequency-swept n.m.d.r. spectra of the vinyl protons of* (I). Numbers below the computed spectrum correspond to the computed transition frequencies, downfield from Me_4Si, minus 300 c./sec.

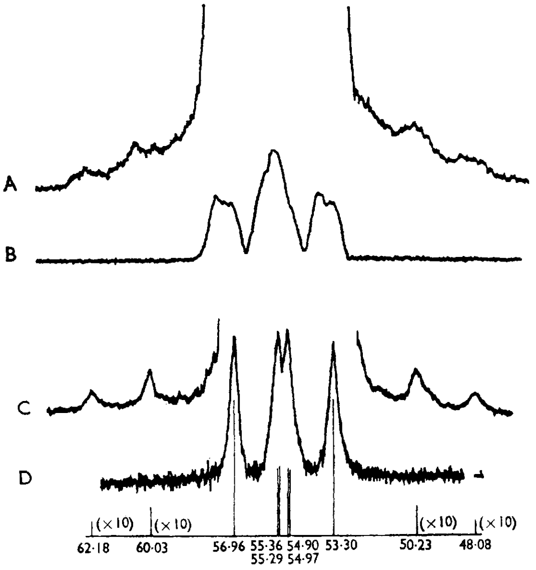


FIGURE 2. A *and* B *are normal n.m.r. spectra of the vinyl protons of* (II). C *and* D *are frequency-swept n.m.d.r. spectra of the vinyl protons of* (II). Numbers below the computed spectrum correspond to the computed transition frequencies, downfield from Me_4Si, minus 300 c./sec.

Agreement between the ^{13}C–H satellite spectral analysis results and those arising from the normal spectral analyses, is satisfactory (Table). The

TABLE

Proton–proton coupling in (I) *and* (II)

	(I)		(II)	
	^{12}C–H Analysis[a]	^{13}C–H Analysis[b,c]	^{12}C–H Analysis[a]	^{13}C–H Analysis[c,d]
$\|J_{2,3}\|$	5·28 cps	5·2 cps	5·77 cps	5·8 cps
$J_{1,2} = J_{3,4}$	+2·85	|2·75|	+2·89	|2·95|
$J_{2,4} = J_{1,3}$	+0·99	|1·1|	+0·77	
$\|J_{1,4}\|$	1·85		1·12	

[a] Parameters are thought to be accurate to ±0·1 c./sec. [b] Ref. 1c gives 5·05, 2·70, and 0·95 c./sec., respectively for these parameters. [c] 1st order analysis parameters. They are accurate probably to ±0·3 c./sec. [d] Ref. 1c.

‡ Where ν_{TMS} is the resonance frequency of Me_4Si.

bridgehead proton couplings ($J_{1,4}$) in (I) and (II) are of considerable magnitudes.

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