

BRIDGEHEAD $^1J(^{13}\text{C-H})$ VALUES IN 1,8-DISUBSTITUTED 1a,2,7,7a-TETRA-HYDRO-1,2,7-METHENO-1H-CYCLOPROPA[b]NAPHTHALENE COMPOUNDS

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The value of the bridgehead $^{13}\text{C-H}$ coupling constant tends to increase as the degree of "strain" increases in cyclic hydrocarbons. Thus, in the highly "strained" 1,3-dimethyltricyclo[1,1,1,0^{4,5}]pentane, the bridgehead $J(^{13}\text{C-H})$ value is 212 Hz¹ and in the slightly less "strained" bicyclo[1,1,0]butane, the bridgehead $^{13}\text{C-H}$ coupling is c. 200 Hz.² In both of these compounds the bridgehead proton is attached to two three-membered rings. When the bridgehead proton is common to two four-membered rings, such as in cubane³ and bicyclo[1,1,1]pentane,² the coupling constant is c. 160 Hz. In "unstrained" systems such as methane⁴ and cyclohexane^{5,6} the value is c. 125 Hz.

Therefore the $^1J(^{13}\text{C-H})$ values of the bridgehead protons of derivatives of 1a,2,7,7a-tetrahydro-1,2,7-metheno-1H-cyclopropa[b]naphthalene (1)^{7,8} were of interest and these values were determined on the compounds (1a-e). The results are given in Table 1. The corresponding values for the methyl groups are included.

The value of c. 181 Hz observed for the H 1a protons is as expected for a proton at a bridgehead position common to three- and four-membered rings, being smaller than the corresponding value in bicyclo[1,1,0]butane (c. 200 Hz)² and larger than the value in bicyclo[1,1,1]pentane² and cubane systems (c. 160 Hz).³ Also the value of c. 149 Hz observed for the H 2 proton is as expected for a proton at a bridgehead position common to four- and five-membered rings, being smaller than the value observed in bicyclo[1,1,1]pentane² and cubane³ systems (c. 160 Hz).

The introduction of methyl substituents or the replacing of either of the phenyl rings with a 4-pyridyl ring did not alter the bridgehead $^1J(^{13}\text{C-H})$ values. The corresponding value of the methyl groups is not altered from the normal values observed for these groups in hydrocarbons.

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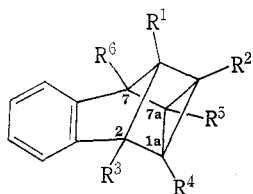
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	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
(1a)	Ph	Ph	H	H	H	H
(1b)	Ph	Ph	H	Me	Me	H
(1c)	Ph	Ph	Me	H	H	Me
(1d)	4-pyridyl	Ph	H	H	H	H
(1e)	Ph	4-pyridyl	H	H	H	H

TABLE 1

 $^1J(^{13}\text{C}-\text{H})$ VALUES (Hz)(Values believed to be correct to within ± 2 Hz)

Compound	Solvent	C 1a-H	C 2-H	C 1a-CH ₃	C 2-CH ₃
(1a) ^a	CCl ₄	182	149		
(1b) ^b	CCl ₄		148	126	
(1c) ^b	CCl ₄	181			125
(1d) ^a	CDCl ₃	181	150		
(1e) ^a	CDCl ₃	183	150		

^a Coupling constants determined from measurements involving the high field half of the appropriate spectrum.

^b Coupling constants determined from measurements involving both the high field and low field sections of the appropriate spectrum.

Experimental

The $^1J(^{13}\text{C}-\text{H})$ values were determined on 15–20% w/v solutions in the solvent specified in Table 1. A Varian A-60 spectrometer and C-1024 time averaging computer was employed. The number of scans per individual determination was in the range 350–500. Tetramethylsilane was used as the internal "trigger peak" with (1b) and (1c), and dichloromethane with (1a), (1d), and (1e). The spectra were calibrated by examination, under identical spectrometer and "time averaging computer" settings, of a "standard" solution of a mixture of compounds having peaks in the region of interest. The "standard" sample was calibrated by the usual side-band technique. The probe temperature was 30°. The splitting patterns of the appropriate spectrum were as expected from a prior knowledge of the proton-proton coupling constants.⁷ A similar case concerning the ^{13}C satellite spectra of 4-substituted pyridines has been discussed.⁹

Acknowledgments

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