Carbon-13 Coupling Constants and Chemical Shifts in Strained and Crowded Olefins

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Summary The ^{13}C chemical shifts and ^{13}C–H coupling constants of 1,1-disubstituted and trisubstituted olefinic hydrocarbons have been examined to elucidate the influence of ring strain and bulky substituents on these parameters.

There is continuing interest in the correlation of ^{13}C–H coupling constants and ^{13}C chemical shifts[1,2] with the molecular structure of olefins.[3,4] We now report the ^{13}C spectra of selected 1,1-disubstituted and trisubstituted olefins. These spectra were obtained on a Varian XL-100-15 operating at 25·2 MHz in the Fourier transform mode of operation. The precision of the measurements of the chemical shifts and coupling constants (see Figure and Table) is 0·1 p.p.m. and 0·5 Hz, respectively.

Table. *Chemical shifts*[a] *and* J_{CH} *of* 1,1-*disubstituted olefins*

$$\underset{\epsilon}{C}—\underset{\delta}{C}—\underset{\gamma}{C}—\underset{\beta}{C}=\underset{\alpha}{C}$$

	Chemical shifts					J_{CH}	
Compound	C_α	C_β	C_γ	C_δ	C_ε	=C–H	H–C–C=CH_2
1,1-Di-t-butylethylene ..	−108·6	−163·8	−37·5	−32·5		151·9	
Methylenecyclobutane[b] ..	−105·2	−149·8	−32·3	−17·2		154·9	
Methylenecyclopentane[b] ..	−105·2	−152·3	−33·3	−27·1		154·2	4·2
Methylenecyclohexane[b] ..	−106·9	−149·2	−35·8	−28·8	−26·9	153·5	5·2
Methylenecycloheptane ..	−110·9	−151·2	−36·6	−29·0	−30·0	153·4	5·5

[a] Chemical shifts, in p.p.m., with respect to Me_4Si. [b] Chemical shift data in agreement with published[2a] values.

The methyl carbons of trimethylethylene gave rise to a well-resolved trio of quartets; the methyl at −13·3 p.p.m. clearly showed a distinct doublet splitting by the single hydrogen on the geminal olefinic carbon; the methyl at —17·1 p.p.m. was assigned on the basis of the greater fine structure in its absorption, presumably due to coupling with the *trans* olefinic proton. All the assignments reported here are in agreement with published[2a] chemical shift data for analogous compounds.

The olefinic J_{CH} for the methylenecycloalkanes reported here and values for cyclic olefins in the literature[2e] are all greater than 153 Hz. However, for 1,1-di-t-butylethylene, trimethylethylene, and tri-t-butylethylene the coupling constants are distinctly lower, and the value for the latter compound, 143·2 Hz, is the smallest olefinic J_{CH} known. These results are consistent with a dominant influence of steric compression of the olefinic hydrogens by geminal or *cis* vicinal alkyl groups giving low J_{CH} values, with larger effects for larger alkyl groups. This is supported by the known values 150·4 and 149·4 Hz respectively for *cis*- and *trans*-1,2-di-t-butylethylenes.[2e] The methylenecycloalkanes have great differences in angle strain, but their lack of

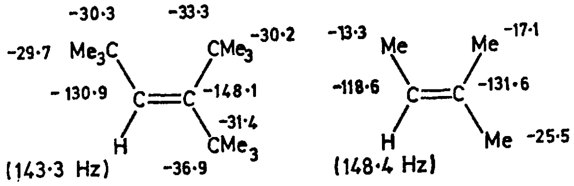

Figure. ^{13}C *Chemical shifts and olefinic* J_{CH} *for tri*-t-*butylethylene and trimethylethylene, chemical shifts in p.p.m. with respect to* Me_4Si.

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variation in the olefinic J_{CH} indicate that they are free of the effects of steric compression of the olefinic hydrogen.

The value of 148·8 Hz for the coupling constant of trimethylethylene should be compared with the value of 156·2 Hz reported[5] for the olefinic J_{CH} for the bridgehead double bond in bicyclo[3,3,1]non-1-ene. This double bond is highly strained but there is no steric compression of the olefinic hydrogen and the coupling constant is the same as that of cyclohexene.

The most notable feature of the chemical shifts is the large deshielding of the carbons bearing two bulky substituents. The full interpretation of this effect and the complicated trends among the ring carbons of the methylenecycloalkanes must await refinements in the theory of chemical shifts.[6]

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