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Angular Dependence of "Electron-Coupled" Proton Interactions in CH_2 Groups

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Experimental and theoretical studies have been made of the dependence upon HCH angle of the electron-coupled proton-proton interactions in CH_2 groups. A valence-bond approximation is used in the theoretical treatment, which predicts that the coupling constant A_{gem}^{HH} decreases from 32 cps to 0 cps for HCH angles of 100° to 125°. For angles greater than 125°, A_{gem}^{HH} is predicted to be negative.

Experimental values of A_{gem}^{HH} have been obtained from analyses of the proton magnetic-resonance spectra of a number of compounds, including several partially deuterated species. Insofar as the HCH angles are known in these compounds, there is good agreement between the theoretical and experimental coupling constants, especially for angles smaller than 120°, for which A_{gem}^{HH} changes more rapidly with angle. Moreover, a negative value is found experimentally for A_{gem}^{HH} in vinyl bromide at an HCH angle which is approximately that at which the theory predicts the coupling to become negative. The substituted ethylenes constitute the largest group of compounds studied experimentally. In them, A_{gem}^{HH} has been found to vary from 3.2 cps to —1.8 cps, while the A_{cis}^{HH} values range from 6.9 cps to 12 cps and the A_{trans}^{HH} from 14.3 cps to 18.4 cps. The various results presented indicate that the value of the coupling constant can serve as a measure of the HCH angle. However, further work is needed to confirm the reliability of the method and investigate the effects of substituent perturbations.