The Sign of Unusually Large $^{4}J_{\rm H,H}$ Values in Bridged Cyclobutane Systems

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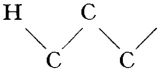
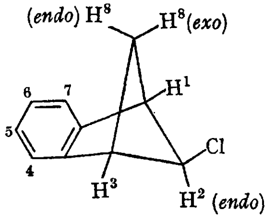
SINCE Barfield[1] proposed a theory of the long-range spin coupling between two protons across four single bonds, it has long been desirable to determine the signs of unusually large $^{4}J_{\rm H,H}$ values observed in several bridged cyclobutane systems.[2–4] These large ^{4}J values have been explained by the following mechanisms: (1) a "W-plan" arrangement[1,5] in a  fragment; (2) the overlap of back-side lobes of two C-H bonds participating in the coupling;[2,3,6] and (3) the double or triple paths between the two interacting protons.[1,7] The sign and magnitude of ^{4}J have been determined for some monocyclobutane derivatives ($+0{\cdot}5$ to $+2{\cdot}5$ Hz for $J_{1,3}$ in a "W-plan" arrangement),[8] but not for bridged cyclobutanes.



(I)

If the sign of a large ^{4}J for a bicyclo[2,1,1]hexane derivative is known, all the signs of the ^{4}J's observed so far can be deduced because the absolute ^{4}J values increase as the ring system goes from monocyclobutanes[8] to the most strained tricyclo[1,1,1]pentane.[2–4] We report here the determination of the sign of ^{4}J in 2-*exo*-chlorobenzobicyclo[2,1,1]hexene (I)† as a model compound.

Standard double-resonance techniques[9]‡ with H(1) and H(3) decoupled from the other protons in addition, demonstrated that $^{4}J_{2\text{-}endo,\,8\text{-}endo} = +\ 7{\cdot}4$, $^{4}J_{2\text{-}endo,\,8\text{-}exo} = -\ 0{\cdot}2_{5}$, and $^{2}J_{8\text{-}endo,\,8\text{-}exo} = -\ 6{\cdot}5_{5}$ Hz; the small magnitude of $^{4}J_{2\text{-}endo,\,8\text{-}exo}$ was determined by "line-transfer" experiments.[10] The relative signs are established by the experiments and the absolute signs are based on the assumption that the geminal $^{2}J_{8\text{-}endo,\,8\text{-}exo}$ is negative, as generally accepted.[8,11]

The present finding suggests that all unusually large ^{4}J values found for bridged cyclobutanes are positive, and may provide useful information for more theoretical work, although the three mechanisms described earlier are believed to play important roles in the couplings.

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† This compound was prepared by treatment of *endo*-2-benzobicyclo[2,1,1]hexenic acid (H. Tanida and Y. Hata, *J. Amer. Chem. Soc.*, 1966, **88**, 4289) with lead tetra-acetate and lithium chloride according to Kochi's procedure (J. K. Kochi, *J. Org. Chem.*, 1965, **30**, 3265). The numbering used in this paper is indicated in the diagram.

‡ The ^{1}H n.m.r., ^{1}H n.m.d.r., and ^{1}H n.m.t.r. spectra in CCl_4 were recorded on a Varian HA-100 spectrometer operating at 100 MHz with two Hewlett-Packard HP–200ABR audio-oscillators in the frequency-swept and internal Me_4Si-locked mode. Calibration of the charts was carried out by direct readings of frequencies by using a Hewlett–Packard HP-5212A electronic counter, accuracies to 0·1 Hz.

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