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CHIRAL RECOGNITION ACROSS THE CARBON-CARBON TRIPLE BOND: EVIDENCE FROM ^{13}C N.M.R. SPECTROSCOPY

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Magnetic shielding non-equivalence (anisochrony) due to diastereotopic[1] discrimination across the carbon-carbon single bond in substituted ethanes $CXYZ\text{-}CU_2V$ is a subject of continuing interest.[1,2] We report here the first observation of anisochrony of nuclei U_a and U_b in substituted but-2-ynes $CXYZ\text{-}C{\equiv}C\text{-}CU_aU_bV$. In addition, resolution of the individual spectra of the meso and racemic isomers of a but-2-yne of type $CXYZ\text{-}C{\equiv}C\text{-}CXYZ$ is described.

At ambient spectrometer temperature (ca.30°C) and under conditions of proton modulated decoupling the diastereotopic methyl carbon nuclei of racemic 2-chloro-5-methylhex-3-yne (1.75M in deuteriochloroform) exhibit an anisochrony of magnitude 0.011 p.p.m. as shown in the Figure.[3] On dilution from 3M to 1.5M no variation in line separation was observed. Further, the symmetric line shapes and absence of splittings in the C-1 and C-5 signals eliminate the possibility that the observed anisochrony in the isopropyl methyl carbons is due to chiral neighbours in diastereomeric complexes in solution. Previous attempts[4] to observe proton anisochrony in related molecules have been unsuccessful principally because the spectral dispersion of protons is typically an order of magnitude smaller than that for carbon.

We have also resolved the proton decoupled ^{13}C n.m.r. spectrum

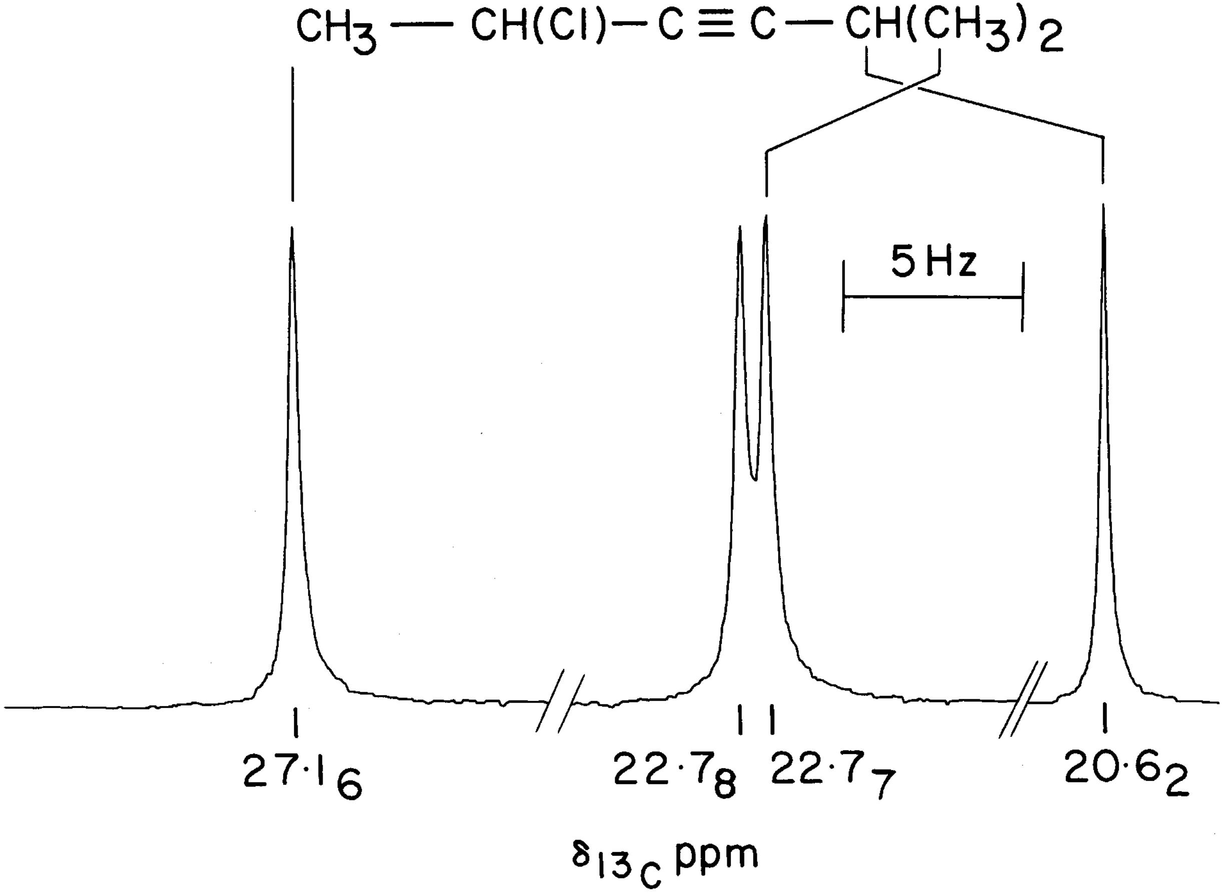

Figure: An expansion of the ^{13}C n.m.r. spectrum of the high field region in 2-chloro-5-methylhex-3-yne.

of a mixture of meso and racemic isomers of 2,5-dichlorohex-3-yne (1.5M in deuteriochloroform). The methyl carbon signals of the two isomers are separated by 0.019 p.p.m. and are readily resolved. The methine carbon atoms reproducibly occurred as a broad resonance with a shoulder corresponding to a line separation of ca. 0.011 p.p.m., while the acetylenic carbon atoms of the meso and racemic isomers exhibited distinct resonances separated by 0.008 p.p.m.[5] We have made no attempt to assign these resonances to the individual isomers which were deduced to be in the ratio 0.8:1. Splittings due to spin couplings with chlorine nuclei can be discounted[6] as can differential shieldings resulting from molecules of different molecular weight containing ^{35}Cl and ^{37}Cl isotopes. Evidence for the latter point is provided by the observation of single resonances for all carbon atoms in 2-chloro-5-methylhex-3-yne.

It is well known[7-9] that nuclear shieldings distinguish meso and racemic isomers of substituted ethanes. The use of ^{13}C n.m.r. spectroscopy to distinguish meso and racemic isomers in which the chiral moieties interact across a carbon-carbon triple bond is of analytical significance and is now clearly established. A theoretical framework for interpreting anisochrony due to chiral discrimination has been developed.[10]

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References and Notes

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3. These studies were performed at 67.89 MHz using a Bruker HFX-270 spectrometer. The deuteriochloroform provided the lock signal while the frequency was digitally controlled using a Nicolet 1180 computer and Bruker interface. Proton decoupling was accomplished using a Bruker BSV-3BX broadband decoupler with the carrier frequency set in the centre of the spectrum under study. A spectral window of 1000 Hz was accumulated into 32K of memory (100-500 pulses) using a repetition rate of 16.385 sec. These conditions provide a computer resolution of 0.061 Hz/bit and adequate relaxation between pulses to facilitate use of a 90° pulse. The error in shifts is thus estimated at ± 0.12 Hz ≡ 0.002 p.p.m. While measurement at high field may not be essential it certainly is an aid to resolution. We must emphasize the need for adequate spectral and computer resolution in determining these data. Chemical shift assignments, based on both signal multiplicity and chemical shift criteria, are as follows: (δ p.p.m. values from internal TMS) 2-chloro-5-methylhex-3-yne, C-1, 27.1_6; C-2, 44.6_5; C-3, 91.6_5; C-4, 79.2_2; C-5, 20.6_2; and C-6, 22.7_7 and 22.7_8 p.p.m., and 2,5-dichlorohex-3-yne, C-1, 26.2_7 and 26.2_5; C-2, 43.3_1 and 43.3_2; and C-3, 84.5_7 and 84.5_6 p.p.m.
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