

Structural Dependence of Long Range Carbon-Hydrogen Coupling in Camphor

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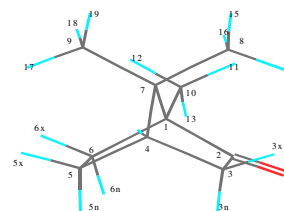
Abstract: The use of heteronuclear correlation techniques such as Heteronuclear Multiple Bond Coherence (HMBC) allows the individual hydrogen couplings to a particular carbon to be readily distinguished, since they are differentiated by their ^1H shift in the second dimension. This connectivity information normally leads to unambiguous assignment of carbon and hydrogen spectra, and consequent structural identification, even for complex compounds. In view of the importance of these correlations in interpreting chemical shifts of rigid polycyclic systems, we have reinvestigated their angular dependence on camphor, calculating its geometry and chemical shifts by DFT methods. Our results reveal that carbon-hydrogen couplings are consistent with dihedral angle correlations. However, there are small discrepancies between HMBC and Fully Coupled Correlation (FUCOUP) results for camphor. On the basis of the results, we can argue that the carbon-hydrogen correlation peaks are observed when the dihedral angle is higher than 125° or lower than 60° . No correlation peaks were found for dihedral angles between 60° and 125° . In the case of methyl groups, when at least one of the hydrogens is in the condition mentioned, correlation occurs. HMBC spectra indicated more correlation peaks than FUCOUP, revealing all the correlations that would be expected from angular dependence. Correlations in the vicinity of 120° dihedral angles must be interpreted with caution, since there are other factors affecting the magnitudes of coupling constants, such as bond lengths, which may become important in borderline situations.

The use of heteronuclear correlation techniques such as Heteronuclear Multiple Bond Coherence (HMBC) allows the individual hydrogen couplings to a particular carbon to be readily distinguished, since they are differentiated by their ^1H shift in the second dimension.¹ This connectivity information normally leads to unambiguous assignment of carbon and hydrogen spectra, and consequent structural identification, even for complex compounds.

In view of the importance of these correlations in interpreting chemical shifts of rigid polycyclic systems, we have reinvestigated their angular dependence in camphor, calculating its geometry and chemical shifts by DFT methods. Our results reveal that carbon-hydrogen

couplings are consistent with dihedral angle correlations.² However, there are small discrepancies between HMBC and Fully Coupled Correlation (FUCOUP) results for camphor.¹

Figure 1. Camphor ($\text{C}_{10}\text{H}_{16}\text{O}$)



Theoretical calculations were run using Gaussian 98³ program with the GIAO procedure and B3LYP/6-31G(d,p) level. All HMBC spectra

were acquired with 10 mg of camphor in a 5 mm o.d. tube using CDCl_3 as solvent and TMS as reference on a Varian Unity Plus 300MHz spectrometer (299.96 MHz for ^1H and 75.43MHz for ^{13}C) at 303K. Since camphor has coupling constants with different magnitudes, a J array (J=3Hz, 6Hz and 8Hz) and cuts in different heights were performed in the HMBC spectra in order to observe all correlations.

HMBC experiments were done in the following conditions: $j_{\text{nxh}}=3\text{Hz}$, $j_{1\text{xh}}=140\text{Hz}$, $at=0.199\text{s}$, $np=1\text{K}$, $sw(\text{F1})=20000.0\text{Hz}$, $sw(\text{F2})=2575.5\text{Hz}$, $nt=32$, $ni=256$, $d1=2\text{s}$, gaussian function in F1 and F2, linear prediction($t1$)= $4ni$, $fn1=np$, $fn=2np$, $pw=90^\circ$; $j_{\text{nxh}}=6\text{Hz}$,

$j_{1\text{xh}}=140\text{Hz}$, $at=0.211\text{s}$, $np=1\text{K}$, $sw(\text{F1})=18099.5\text{Hz}$, $sw(\text{F2})=2430.3\text{Hz}$, $nt=8$, $ni=512$, $d1=2\text{s}$, $fn=np$, $fn1=2np$, gaussian function in F1 and F2, linear prediction ($t1$)= $4ni$, $pw=90^\circ$; $j_{\text{nxh}}=8\text{Hz}$ (the same parameters for $j_{\text{nxh}}=6\text{Hz}$ were used).

On the basis of the results, we can argue that the carbon-hydrogen correlation peaks are observed when the dihedral angle is higher than 125° or lower than 60° . No correlation peaks were found for dihedral angles between 60° and 125° . In the case of methyl groups, when at least one of the hydrogens is in the condition mentioned, correlation occurs. HMBC spectra indicated more correlation peaks than reference 1, revealing all the correlations that would be expected from the angular dependence.²

Table 1. Camphor dihedral angles (calculated by Gaussian 98 program)/cross peaks

H _{3n}	(122.5)	---	---	---	(47.5)*	---	(155.2)*	---	---	---
H _{3x}	119.6	---	---	---	(170.4)*	---	81.9	---	---	---
H ₄	(179.9)*	(160.9)*	---	---	---	(162)*	---	62.1	61.3	---
H _{5n}	122.4	---	(49.9)	---	---	---	(157.6)*	---	---	---
H _{5x}	117.5	---	(169.4)*	---	---	---	82.9	---	---	---
H _{6n}	---	(50.8)	---	118.8	---	---	(154.8)*	---	---	73.9
H _{6x}	---	(168.7)*	---	120.7	---	---	87.4	---	---	(43.9)
H ₈	(168.5)*	---	---	(178.8)*	---	---	---	---	(174.6)*	---
H ₉	(172.8)*	---	---	(175.2)*	---	---	---	(178.8)*	---	---
H ₁₀	---	(175.5)*	---	---	---	(177.8)*	(174.2)	---	---	---

* = cross peaks in reference 1 (FUCOUP spectrum)

() = cross peaks in HMBC spectra

Correlations in the vicinity of 120° dihedral angles must be interpreted with caution, since there are other factors that affect the magnitudes of coupling constants, such as

bond lengths, which may become important in borderline situations.

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