The Complete Proton Nuclear Magnetic Resonance Analysis of Norcamphor

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Abstract: All of the proton nmr parameters of norcamphor (1) have been obtained by a high resolution study of various deuterated norcamphor derivatives. These parameters are discussed in terms of the geometry of norcamphor as determined by force field calculations.

Most of the research concerning the proton nmr of norbornane derivatives has dealt with multinuclei systems which exhibited highly complex spectra impossible to analyze completely.[2] In many cases, a first-order approximation has been taken which unavoidably leads to errors owing to (1) lack of resolution of multiplets and (2) the fact that first-order measurements are not identical with the J values in second-order systems. Another difficulty in obtaining proton nmr parameters of norbornane derivatives has been that in symmetrical systems[2a,b,d,e] deceptively simple spectra may arise whose analysis not only does not allow the derivation of some parameters but also can give faulty conclusions.

A few recent examples have shown that in some suitably chosen norbornane systems, long-range couplings can be observed[3-6] in addition to the well-known "W"-type couplings. These examples suggest that possibly other long-range couplings exist. Thus, we considered it desirable to perform a complete proton nmr analysis of some norbornane derivative to ascertain precisely which coupling constants were not zero.

In choosing this norbornane derivative, we sought an unsymmetrical system (because of restriction 2 above) which could be deuterated selectively in various positions. Our choice for this model compound was norcamphor (1). With two enolizable hydrogens and with several methods available for synthesis, there would be ample opportunity to prepare various norcamphor derivatives deuterated in several specific positions.

Synthesis of the Deuterated Norcamphor Derivatives. Schemes I, II, and III show the synthetic sequences giving the deuterated norcamphor derivatives (1a–f) studied. In Scheme I, endo-5-norbornenyl acetate (2) was allowed to react with dideuteriodiimide[7] to give 3. Saponification and subsequent Sarett oxidation[8] gave 1a. Exchange of the two 3-protons[9] gave 1b.
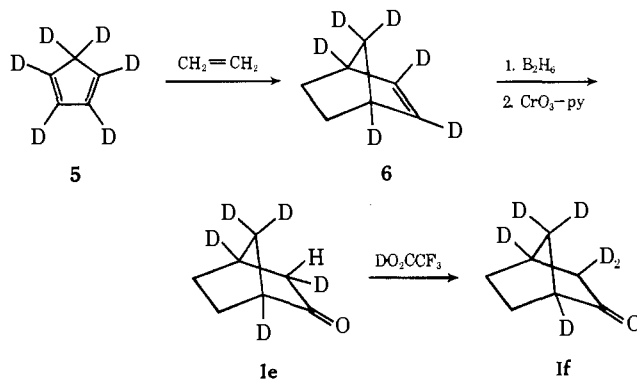
Scheme I
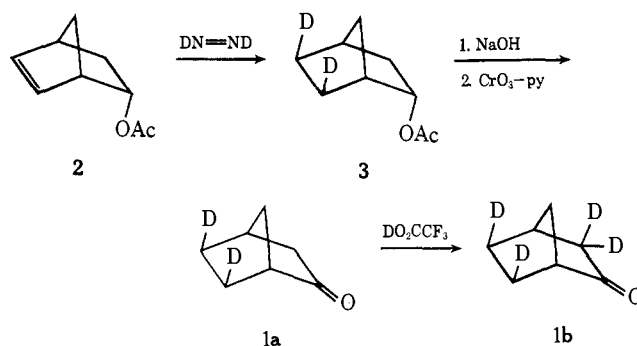
Scheme II
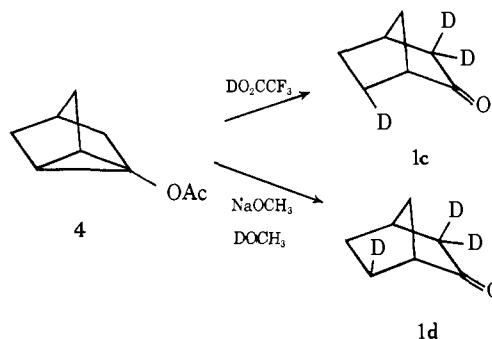
Scheme III

In Scheme II, 1-nortricyclyl acetate (4), prepared according to the procedure of Hart,[10] was treated with

(1) Robert A. Welch Undergraduate Fellow, 1970–1974.
(2) For examples, see the following and references cited therein: (a) A. P. Marchand and J. E. Rose, J. Amer. Chem. Soc., 90, 3724 (1968); (b) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, ibid., 90, 3721 (1968); (c) K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, ibid., 89, 2401 (1967); (d) P. Laszlo and P. v. R. Schleyer, ibid., 86, 1171 (1964); (e) N. Kamezawa and K. Sakashita, Org. Magn. Resonance, 1, 405 (1969).
(3) G. F. Hambly, J. Leitch, P. Yates, and S. C. Nyburg, Can. J. Chem., 51, 4076 (1973).
(4) G. Chalier, D. Gagnaire, and A. Rassat, Bull. Soc. Chim. Fr., 387 (1969).
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trifluoroacetic acid-O-d to give **1c**. The 6-epimer **1d**[11] was prepared by treating **4** with sodium methoxide in methanol-O-d.

In Scheme III, perdeuteriocyclopentadiene (**5**), prepared according to the procedure of Anet,[12] was treated with ethylene[13] to give **6**. Hydroboration[14] of **6** and subsequent Sarett oxidation[8] gave **1e**. Exchange[9] of the 3-exo-proton gave **1f**.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus. Mass spectral analyses were performed on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. The proton nmr spectra were recorded on a JEOL PS-100 nmr spectrometer, using $\sim 20\%$ solutions of the appropriately deuterated sample in deuteriochloroform with 1% v/v tetramethylsilane internal standard (except for **1d**, which was 5%), utilizing internal lock field sweep mode. Lanthanide shift reagent Eu(fod)$_3$ was purchased from Norell Chemical Co.

exo,exo-5,6-Dideuterionorcamphor (**1a**). To a stirring mixture of 12.36 g of *endo*-5-norbornenyl acetate (**2**) (purchased from Aldrich Chemical Co., Milwaukee, Wis.), 162 g of potassium azodicarboxylate, and 240 ml of methanol-O-d was added dropwise 132 g of acetic acid-O-d over a period of 1 hr.[7] The reaction mixture was then diluted with 1 l. of water and extracted with three 50-ml portions of ether. The combined ethereal extracts were washed with aqueous sodium bicarbonate and brine, dried (magnesium sulfate), and concentrated by distillation to give 12.28 g (97%) of oil (**3**). This crude product without further purification was stirred overnight in 100 ml of 5% aqueous sodium hydroxide. The mixture was then extracted with three 50-ml portions of ether. The combined ethereal extracts were washed, dried (magnesium sulfate), and concentrated to give 9.14 g of a semisolid. This crude alcohol was added to a pyridine–chromium trioxide complex[8] (prepared from 475 ml of pyridine and 40 g of chromium trioxide). The resulting mixture was stirred for 34 hr, poured into 1 l. of water, and extracted with five 100-ml portions of ether. The combined ethereal extracts were washed with 475 ml of 20% aqueous sulfuric acid and then with 500 ml of water, dried (magnesium sulfate), concentrated under reduced pressure, and sublimed (110°, 30 mm) to give 6.20 g of pure **1a** for an overall yield of 68%, mp 88–91°. Mass spectral analysis: 86.6% d_2, 8.9% d_1, 4.4% d_0.

3,3,*exo,exo*-5,6-Tetradeuterionorcamphor (**1b**). Two exchanges were necessary for complete reaction. A solution of 1.22 g of **1a** and trifluoroacetic acid-O-d[9] (prepared by the cautious addition of 2.2 g of trifluoroacetic anhydride to 2.7 g of deuterium oxide) was heated at 125° in a sealed tube for 12 days. The solution was then added to a cold mixture of 6 ml of water and 6.0 g of potassium carbonate and extracted with 40 ml of pentane. The pentane extract was dried (magnesium sulfate) and concentrated to give a pure sample. This overall procedure was repeated. The final product **1b** was obtained in 33% yield (0.40 g). Mass spectral analysis: 85.5% d_4, 10.0% d_3, 4.7% d_2.

3,3,*endo*-6-Trideuterionorcamphor (**1c**). 1-Nortricyclyl acetate (**4**) (0.46 g), prepared according to the procedure of Hart,[10] was treated with trifluoroacetic acid-O-d[11] (prepared from 5.56 ml of trifluoroacetic anhydride and 10 ml of deuterium oxide) at 125° for 3 days. Work-up as for **1b** gave 0.19 g (56%) of pure **1c** after sublimation. Mass spectral analysis: 88.2% d_3, 7.8% d_2, 4.0% d_1.

3,3,*exo*-6-Trideuterionorcamphor (**1d**). 1-Nortricyclyl acetate (0.95 g) was heated[11] in a solution of sodium methoxide in methanol-O-d (prepared by the reaction of 1 g of sodium in 30 ml of methanol-O-d) in a sealed tube at 125° for 3 days. The mixture was extracted with three 20-ml portions of pentane. The pentane extracts were dried (magnesium sulfate) and concentrated by distillation. The crude product was sublimed to give 0.053 g (8%) of **1d**. No mass spectral analysis was performed, owing to the small amount of material.

Perdeuteriocyclopentadiene (**5**) dimer was prepared according to the procedure of Anet.[12]

(11) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **88**, 3354 (1966).

(12) F. A. L. Anet, H. H. Lee, and J. L. Submeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967).

(13) J. Meinwald and N. J. Hudak, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 738.

(14) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

1,2,3,4,7,7-Hexadeuterionorbornene (**6**) was prepared from **5** and ethylene according to the procedure of Meinwald.[13]

1,*endo*-3,4,7,7-Pentadeuterionorcamphor (**1e**). Diborane, generated by the dropwise addition of a solution of 25 ml of boron trifluoride etherate in 75 ml of diglyme to a solution of 4.0 g of sodium borohydride in 100 ml of diglyme over a period of 2 hr, was swept through a solution of 2.96 g of **6** in 150 ml of dry ether. To the resulting solution was added Sarett reagent[8] (prepared from 15.0 g of chromium trioxide and 170 ml of pyridine). After 6 hr of stirring, the mixture was poured over 750 ml of water and extracted with two 250-ml portions of ether. The combined ethereal extracts were washed with two 150-ml portions of 20% aqueous sulfuric acid and with 150 ml of water, dried (magnesium sulfate), and concentrated to a crude oil. This oil (mostly deuterated norbornyl alcohol) was recycled through another Sarett oxidation and worked up as before to give 1.28 g (38%) of **1e**. Sublimation gave a pure sample. Mass spectral analysis: 91% d_5, 9% d_4.

1,3,3,4,7,7-Hexadeuterionorcamphor (**1f**) was prepared in 50% yield from **1e** using trifluoroacetic acid-O-d as before for **1b**, except that only one exchange was necessary. Mass spectral analysis: 95% d_6, 4% d_5.
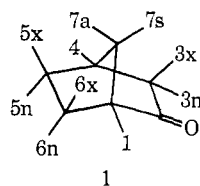
Nmr Analysis

Coupling constants obtained in this study appear in Table I, and chemical shifts appear in Table II. Each of these nmr parameters was obtained by utilizing the iterative routine of the LAOCOON III program.[15] All coupling constants were obtained by using only distinct transitions; no J values appear in Table I which were "approximated" from "apparently broadened" signals (however, *vide infra* regarding **1d** whose inferior resolution precluded the precise measurement of three J values). Thus, the J values in Table I are real and their accuracies are reflected by the respective probable errors. Owing to the tightly coupled nature of the nmr spectra, choice of signs for the J values was possible; different sign possibilities did not allow satisfactory simulation. Signs for large ($|J| > 1$ Hz) couplings are regarded as certain and for small ($|J| < 1$ Hz) couplings are regarded as probable.

In the last column of Table I, the best value for each J value is given as the average from each of the respective compounds. Each of the J values given as "0.0" is regarded to be zero within 0.1 Hz, because (1) the resolution of the spectra would have allowed the observation of splitting of 0.1 Hz or less and (2) each J value listed as "0.0" iterated to <0.1 Hz in the LAOCOON analysis.

In this analysis, it was initially believed that the best plan would be first to study the four- and five-spin systems **1e** and **1f** and then to move on to the six- and seven-spin systems **1b–d**. To our chagrin, unambiguous values for J_{5n6x}, J_{5x6n}, J_{5x5n}, and J_{6x6n} could not be obtained from **1e** and **1f** owing to the very similar chemical shifts of the 5x and 6x protons; instead, only the *sums* of J_{5n6x} and J_{5x6n} and of J_{5n5x} and J_{6n6x} could be obtained. Indeed, aside from a few combination bands of low intensity, the spectral pattern for **1e** was identical with that of an AA'BB' pattern. Even for **1f**, whose spectral pattern was more complex, various changes in these J values (± 0.5 Hz) did not significantly change the appearance of the simulated spectrum. However, the following nonzero J values could be unambiguously obtained: J_{5x6x}, J_{5n6n}, and J_{3x5x}.

Next, a study of the six-spin system **1b** was carried out, in which all J values could be unambiguously ob-

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Table I. Proton J Values of Norcamphor (1)

1

| Protons | | | | | J_{xy} taken from[a] | | | | Final J |
x	y	1a[b]	1b	1c	1d	1e	1f	value
1	3n	0.0						0.0
1	3x	0.0						0.0
1	4		+1.23 ± 0.01	+1.19 ± 0.02	+1.10 ± 0.03			+1.17
1	5n		−0.39 ± 0.03	−0.21 ± 0.02	c			−0.30
1	5x			+0.15 ± 0.02	c			+0.15
1	6n		+0.12 ± 0.03		+0.11 ± 0.03			+0.12
1	6x			+4.72 ± 0.02				+4.72
1	7a		+1.18 ± 0.01	+1.22 ± 0.02	+1.16 ± 0.03			+1.19
1	7s		+1.67 ± 0.01	+1.55 ± 0.02	+1.71 ± 0.03			+1.64
3n	3x	−17.64						−17.64
3n	4	0.0						0.0
3n	5n	0.0						0.0
3n	5x	0.0						0.0
3n	6n	0.0						0.0
3n	6x	0.0						0.0
3n	7a	+4.22						+4.22
3n	7s	0.0						0.0
3x	4	+4.76						+4.76
3x	5n	0.0				0.0		0.0
3x	5x	(2.3)[d]				+2.22 ± 0.07		+2.26
3x	6n	0.0				0.0		0.0
3x	6x	0.0				0.0		0.0
3x	7a	0.0						0.0
3x	7s	0.0						0.0
4	5n		+0.17 ± 0.03	+0.08 ± 0.02	c			+0.12
4	5x			+4.21 ± 0.03	+4.39 ± 0.02			+4.30
4	6n		−0.36 ± 0.03		−0.55 ± 0.03			−0.45
4	6x			+0.65 ± 0.03				+0.65
4	7a		+2.10 ± 0.01	+2.09 ± 0.03	+2.13 ± 0.02			+2.10
4	7s		+1.54 ± 0.01	+1.53 ± 0.03	+1.73 ± 0.02			+1.60
5n	5x			−12.44 ± 0.04	−13.10 ± 0.10	−12.68 ± 0.03	−12.95 ± 0.20	−12.79
5n	6n		+9.20 ± 0.02		+9.08 ± 0.02	+9.06 ± 0.06	+9.14 ± 0.02	+9.12
5n	6x			+4.69 ± 0.03		+4.72 ± 0.28	+4.68 ± 0.21	+4.70
5n	7a		−0.03 ± 0.03	−0.14 ± 0.02	−0.13 ± 0.02			−0.10
5n	7s		+2.30 ± 0.03	+1.95 ± 0.02	+2.02 ± 0.02			+2.09
5x	6n				+4.60 ± 0.06	+4.65 ± 0.29	+4.51 ± 0.21	+4.59
5x	6x			+12.19 ± 0.02		+11.86 ± 0.06	+12.09 ± 0.02	+12.05
5x	7a			0.0	0.0			0.0
5x	7s			0.0	0.0			0.0
6n	6x					−12.48 ± 0.29	−12.08 ± 0.21	−12.28
6n	7a		−0.16 ± 0.03		−0.10 ± 0.02			−0.13
6n	7s		+1.98 ± 0.03		+2.08 ± 0.02			+2.03
6x	7a			0.0				0.0
6x	7s			0.0				0.0
7a	7s		−10.16 ± 0.01	−10.16 ± 0.02	−10.13 ± 0.02			−10.15
Rms error, Hz		0.046	0.120	0.125	0.150	0.044		

[a] In Hz, with probable errors as generated in iteration. Signs for large ($|J| > 1$ Hz) are regarded as certain and for smaller couplings are regarded as probable, as determined from the best simulations. Where a blank space occurs, at least one of the involved protons is labeled with deuterium. [b] Only the 3x3n portion of this spectrum was studied. [c] This coupling was apparent from the broadening of the appropriate signals, but lower resolution for 1d did not allow distinct separation of the appropriate signals necessary for accurate determination of this coupling (see text). [d] Value taken from Eu(fod)₃ study of the nondeuterated norcamphor 1.

tained. From 1b, the following additional nonzero J values were obtained: J_{14}, J_{15n}, J_{16n}, J_{17a}, J_{17s}, J_{45n}, J_{46n}, J_{47a}, J_{47s}, J_{5n7a}, J_{5n7s}, J_{6n7a}, J_{6n7s}, and J_{7a7s}.

Next, analysis of 1c and 1d gave the following additional nonzero J values: J_{15x}, J_{16x}, J_{45x}, J_{46x}, J_{5n5x}, J_{5n6x}, and J_{5x6n}. Resolution for 1d was poorer, and three small J values determined in other derivatives could not be accurately determined in 1d. These three J values are noted in Table I.

Now that the values of J_{5n6x}, J_{5x6n}, and J_{5n5x} were known, it was possible to return to 1e and 1f to choose

the correct cases. The values of these three J values which appear for 1e and 1f in Table I are those involving the line assignment combinations that gave agreement of these J values with the respective J values of 1c and 1d. Perhaps significantly, these particular cases for 1e and 1f gave the smallest rms errors. Choice of these cases, of course, also fixed J_{6n6x}. The relatively large probable errors for J_{5n6x}, J_{5x6n}, J_{5n5x}, and J_{6n6x} for 1e and 1f reflect the uncertainty for these J values if obtained *only* from 1e and 1f.

Turning to the 3n3x portion, the spectrum of 1a was

Table II. Chemical Shifts of Norcamphor (1)

| Proton | Chemical shift, δ_{TMS} | |
	This study[a]	Previous studies[b]
1	2.41	2.39
3n	1.73	
3x	1.95	} 1.6, 1.9
4	2.61	2.6
5n	1.41	
5x	1.76[c]	
6n	1.44	
6x	1.76[c]	
7a	1.51	
7s	1.69	

[a] For the compounds **1a-f** δ_{TMS} might vary up to 0.01 for a given proton. [b] Reference 16. [c] For different derivatives the $\Delta(\delta_{TMS})$ for the 5x and 6x protons might be as large as 0.004, with 5x usually downfield.

next analyzed. Being relatively isolated, the 3n3x region could be easily analyzed to give J_{3n3x} and J_{3n7a}. When a small amount of lanthanide shift reagent Eu(fod)$_3$ was added to **1a**, the 3n3x region moved far downfield and appeared as a sharp doubled AB pattern, reflecting the J_{3n3x}, J_{3n7a}, and J_{3x4} couplings. That this pattern remained sharp and further unsplit when far from other potential coupling proton signals (i.e., first-order patterns were guaranteed) precluded further coupling of the 3n and 3x protons.

Finally, the 3n3x region of nondeuterated norcamphor **1** was observed with added Eu(fod)$_3$ to confirm the J_{3x5x} value previously obtained from **1e**.

Each J value thus obtained is consistent for all compounds **1a-f**. The J values which exhibit the greatest variation and probable errors are the geminal couplings, which are typically more sensitive to experimental errors of the assigned transition frequencies in the LAOCOON program.

Regarding the chemical shifts of norcamphor (Table II), our results confirm the partial analysis of norcamphor done by Farnum and Mehta,[16] who assigned the lower field bridgehead signal as H$_4$.

As an example of the type of spectral patterns observed in this study, Figure 1 shows observed and simulated spectra for **1b**.

Force Field Calculations

Table III lists dihedral angles of norcamphor, as determined by force field calculations. The carbonyl internal angle (C$_1$-C$_2$-C$_3$) for these calculations was set at 107°.[3] We calculated the effect on the overall geometry of norcamphor as this internal angle was allowed to vary from 106° (the internal angle of the sp^2-carbon of norbornene) to 116° (the internal angle of the sp^2-carbon of an unstrained cyclic ketone); for all dihedral angles involved in the following discussion, the maximum variation was 1°. These calculations were done by means of the Lothar Schäfer and Wolfgang Shubert Conformational Program (adapted from Lifson and Marshel[17]) with Variable Minimization Routine. Force field constants for the oxygen heteroatom were taken from Allinger[18] and Altona.[19]

(16) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).
(17) S. Lifson and A. Marshel, *J. Chem. Phys.*, **49**, 5116 (1968).
(18) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, Chapter 7.
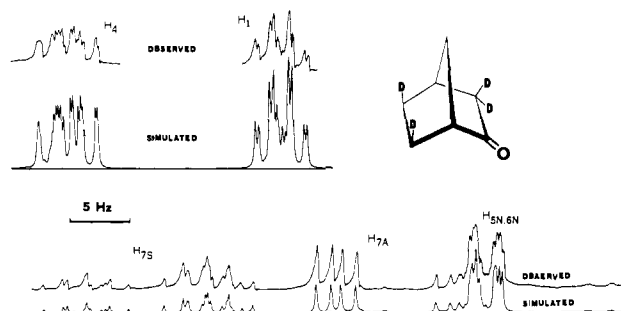
Figure 1. Observed and simulated spectral patterns for **1b**.

Discussion

Symmetry of the Ethylene Bridge. Inspection of Tables I and III confirms that the ethylene bridge is not distorted significantly from mirror symmetry. In particular are to be compared the two $^3J_{trans}$ values (4.70 and 4.59 Hz) and the two involved dihedral angles (for H$_{5x}$-C$_5$-C$_6$-H$_{6n}$ and H$_{5n}$-C$_5$-C$_6$-H$_{6x}$ these are 117.5 ± 1.2°), the two eclipsed H-C-C-H angles[20] (for H$_{5x}$-C$_5$-C$_6$-H$_{6x}$ and H$_{5n}$-C$_5$-C$_6$-H$_{6n}$ these are less than 1.5°), and the dihedral angle of the bridge itself (for C$_1$-C$_6$-C$_5$-C$_4$ this is less than 1°).

Vicinal Couplings. Vicinal J values of Table I are consistent with the involved geometries taken from Table III. As expected from the Karplus relationship,[21] the bridgehead-exo couplings (J_{3x4}, J_{45x}, $J_{16x} \simeq$ 4.6 Hz) with dihedral angles of 42-45° are larger than the bridgehead-7 couplings (J_{17a}, J_{17s}, J_{47a}, $J_{47s} \simeq$ 1.6 Hz) with dihedral angles of 58-61°, which in turn are larger than the bridgehead-endo couplings (J_{3n4}, J_{45n}, $J_{16n} <$ 0.2 Hz) with dihedral angles of 73-76°.

Long-Range Couplings (^4J). The most noticeable of the ^4J values in **1** are the "W" couplings (J_{3x5x} = 2.26, J_{5n7s} = 2.09, J_{6n7s} = 2.03, J_{14} = 1.17, J_{3n7a} = 4.2 Hz), which have been well documented in the literature.[2,22,23] In the present study we were able to confirm the positive sign of this coupling, consistent with theoretical considerations.[24,25]

Next to the "W"-type couplings, the most common ^4J previously observed in norbornanes has been the bridgehead-exo coupling (e.g., J_{15x} or J_{46x} in **1**). Such values have ranged upward to 2 Hz,[2c,3,4,6] primarily in norbornanes with an endo-2,6 bridge that undoubtedly distorts the norbornane skeleton considerably. In the one instance where a sign determination has been made, the J value was positive,[4] in agreement with the present study.

Related to these bridgehead-exo couplings are the bridgehead-endo couplings J_{15n} and J_{46n}. In the present study these J values were suggested to be negative, in contrast to the positive bridgehead-exo J values, notwithstanding the very similar geometries of the bridgehead-exo and of the bridgehead-endo systems (each analogous dihedral angle differs less than 7°).

One other type of long-range coupling in norbornanes

(19) C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, **92**, 1995 (1970).
(20) The nonequivalence of the two $^3J_{cis}$ values is not due to unequal dihedral angles (see ref 5).
(21) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(22) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).
(23) E. W. Garbisch, Jr., *Chem. Commun.*, 332 (1968).
(24) M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971).
(25) M. Barfield and B. Chakrabarti, *Chem. R. v.*, **69**, 757 (1969).

Table III. Dihedral Angles of Norcamphor Determined by Force Field Calculations[a]

System	Angle, deg	System	Angle, deg	System	Angle, deg
C_1-C_2-C_3-C_4	1.0	C_3-C_4-C_5-C_6	72.1	C_7-C_4-C_3-H_{3n}	157.9
C_1-C_2-C_3-H_{3n}	123.2	C_3-C_4-C_5-H_{5x}	169.7	C_7-C_4-C_3-H_{3x}	82.3
C_1-C_2-C_3-H_{3x}	116.8	C_3-C_4-C_5-H_{5n}	51.5	C_7-C_4-C_5-H_{5x}	84.4
C_1-C_6-C_5-C_4	0.6	C_3-C_4-C_7-H_{7a}	176.1	C_7-C_4-C_5-H_{5n}	157.4
C_1-C_6-C_5-H_{5x}	119.8	C_3-C_4-C_7-H_{7s}	63.5	H_1-C_1-C_6-H_{6x}	44.3
C_1-C_6-C_5-H_{5n}	122.7	C_4-C_5-C_6-H_{6x}	117.9	H_1-C_1-C_6-H_{6n}	73.5
C_1-C_7-C_4-C_3	56.1	C_4-C_5-C_6-H_{6n}	124.6	H_1-C_1-C_7-H_{7a}	60.8
C_1-C_7-C_4-C_5	55.8	C_4-C_7-C_1-C_6	55.9	H_1-C_1-C_7-H_{7s}	58.8
C_1-C_7-C_4-H_4	179.8	C_4-C_7-C_1-H_1	178.7	H_{3n}-C_3-C_4-H_4	74.3
C_2-C_1-C_6-C_5[b]	68.0	C_5-C_4-C_3-H_{3n}	53.0	H_{3x}-C_3-C_4-H_4	45.4
C_2-C_1-C_6-H_{6x}[b]	173.9	C_5-C_4-C_3-H_{3x}	172.8	H_4-C_4-C_5-H_{5x}	42.8
C_2-C_1-C_6-H_{6n}[b]	56.1	C_5-C_4-C_7-H_{7a}	64.2	H_4-C_4-C_5-H_{5n}	75.4
C_2-C_1-C_7-C_4	53.8	C_5-C_4-C_7-H_{7s}	175.5	H_4-C_4-C_7-H_{7a}	59.8
C_2-C_1-C_7-H_{7a}	174.2	C_5-C_6-C_1-C_7	34.8	H_4-C_4-C_7-H_{7s}	60.5
C_2-C_1-C_7-H_{7s}	66.1	C_5-C_6-C_1-H_1	162.3	H_{5x}-C_5-C_6-H_{6x}	1.2
C_2-C_3-C_4-C_5	70.0	C_6-C_1-C_7-H_{7a}	64.5	H_{5x}-C_5-C_6-H_{6n}	116.3
C_2-C_3-C_4-C_7	34.9	C_6-C_1-C_7-H_{7s}	175.8	H_{5n}-C_5-C_6-H_{6x}	118.7
C_2-C_3-C_4-H_4	162.7	C_6-C_5-C_4-C_7	33.8	H_{5n}-C_5-C_6-H_{6n}	1.2
C_3-C_2-C_1-C_6	70.1	C_6-C_5-C_4-H_4	161.1		
C_3-C_2-C_1-C_7	32.8	C_7-C_1-C_6-H_{6x}	83.3		
C_3-C_2-C_1-H_1	160.1	C_7-C_1-C_6-H_{6n}	158.9		

[a] The internal angle of the carbonyl (C_1-C_2-C_3) was fixed at 107.0°. Dihedral angles in this table do not vary over 1° as the carbonyl internal angle is varied over the range 106–116°, except where noted. [b] This angle varies up to 5° as the carbonyl internal angle is varied over the range 106–116°.

exists in the literature, the exo–syn coupling (analogous to 5x7s and 6x7s in **1**), which has been reported to be 0.40 Hz in a 7-acetoxynorbornane compound.[5] In the present study thse J values are zero. Possibly the electronegative substituent at the 7-carbon is responsible[24,25] for the finite value of this coupling in the acetoxy compound.

In the present study one more type of long-range coupling was observed, the endo–anti coupling (J_{5n7a} and J_{6n7a}).

Comparison of Observed ⁴J Values with Theoretical Values. Two theoretical studies have appeared which predict the relationship between ⁴J and the two involved dihedral angles, one study using the VB method[25] and the other using the INDO method.[24] The data of the present study do not agree qualitatively with either study, except for the "W" couplings. In particular, both theoretical studies would predict that the smallest ⁴J values in norcamphor (in an algebraic sense) would be J_{5x7a} and J_{6x7a}, which should be negative. In fact, these J values are zero and are larger (in an algebraic sense) than several other ⁴J values in norcamphor. These calculations, however, were done assuming an unstrained system. Additional complications induced in the relatively strained norbornane system may be responsible for departures of observed values from

predicted ⁴J values. Supporting this idea, the J_{14} coupling, which involves an almost perfect "W" with dihedral angles of 179 and 180° and is thus calculated to have the largest ⁴J in **1**, actually has a ⁴J value about half that of the other "W" couplings.[26] The J_{14}-"W" is more strained, and this strain may be responsible for the departure from the general trend.

The present study therefore suggests that extreme care should be exercised in structure elucidations involving ⁴J in aliphatic systems. In the norbornane system itself, it is suggested that at best a *trend* exists whereby the closer a particular geometry is to a "W" configuration, the more likely the coupling is to be substantial, but that arguments based on fine differences in ⁴J are dangerous. Thus, in norbornanes one can depend heavily only on the "W" couplings and to a lesser extent on the "near-W" bridgehead–exo and bridgehead–endo couplings.

(26) Such a small J_{14} is also observed in norbornene and norbornadiene (ref 23).