

# Substituent Chemical Shifts in NMR

## 1—Proton Resonance Spectra and Geometries of Norbornene, Norbornane and Adamantane

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The molecular geometries and proton NMR spectra of norbornene, norbornane and adamantane are reported. The molecular geometries were refined from previous experimental determinations using MNDO and *ab initio* techniques to determine the positions of the hydrogen atoms. No evidence of any *endo-endo* interactions in norbornane was obtained from these calculations.

High-field proton NMR spectra allow the refinement of previous spectral analyses of adamantane and norbornane, and the complete analysis of the olefin decoupled eight spin system of norbornene. The chemical shifts of the parent compounds and cyclohexane under comparable conditions show minor but significant differences from previous values. The methine-methylene coupling in adamantane is 3.30 Hz. The long-range couplings in norbornene were compared with those calculated by FPT/INDO and EHMO/VB methods. Only moderate agreement was obtained and possible reasons for this are examined.

### INTRODUCTION

The influence of substituents on nuclear chemical shifts has been under investigation almost since the original discoveries of NMR.<sup>1,2</sup> Indeed, the term chemical shift refers to the distress of the pioneers in NMR on discovering that the same nucleus in different molecules resonated at different values of the applied field, thus precluding an accurate measurement of the nuclear gyromagnetic ratio.<sup>2</sup>

However, despite the numerous investigations since then, a quantitative interpretation of SCS of even the most studied nucleus, <sup>1</sup>H, is still lacking. The reasons are not difficult to find, as the pioneering investigations of Zurcher in this field demonstrated.<sup>3</sup> He considered the various possible mechanisms influencing protons SCS, which included the substituent magnetic anisotropy, electric field, Van der Waals (steric) effects and also the solvent reaction field, and applied these calculations to the SCS of the C-18 and C-19 methyl groups in steroids of known rigid geometry. The major difficulty which this elegant investigation faced was that only the signals of the methyl groups could be identified and measured accurately at the low applied fields used at this time, and the rapid rotation of the methyl group about the C—C bond largely averaged out the orientational dependence of the SCS. Hence he was unable to obtain a sufficiently diverse set of data to assess accurately the proportions of the different terms.

With modern high-field spectrometers, the complete analysis of the proton spectra of molecules of accurately known, rigid geometry and of sufficient complexity to provide over-determined data sets for analysis of the SCS is now a feasible prospect. Amongst such molecules the adamantane norbornane

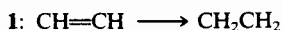
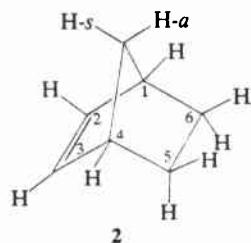
and cyclohexane systems are ideally suited for this type of investigation, and for this reason they have been intensely studied by NMR.<sup>4</sup> Again, because of the complexity of the proton spectra, most of the NMR studies have been concerned with multi- rather than mono-substituted derivatives. In this series of investigations we wished to obtain the SCS of selected functional groups at all the protons in the molecule, and then to analyse the data sets in terms of present theories of SCS. Here we present the proton NMR parameters of the parent molecules adamantane, norbornane and norbornene, the latter requiring full analysis of the eight spin spectrum obtained by decoupling the olefinic protons. We also give the geometries of these molecules, largely taken from previous determinations but refined where necessary by *ab initio* calculations.

The parent molecules all give complex partially resolved proton spectra at lower applied fields, and the chemical shifts quoted previously were either extracted from these partially resolved spectra or, more rigorously, from the spectra of polydeuteriated derivatives. The deuteration studies gave unambiguous assignments of these spectra but, of course, most of the coupling information is lost. The assignments are not in question; we merely wished to obtain more accurate values of the chemical shifts and, where possible, the coupling constants.

For example the low-field (60 MHz) spectrum of adamantane recorded by Fort and Schleyer<sup>5</sup> consists of a high-field doublet due to the methylene protons and a broad shoulder at low field from the methine protons. The observed pattern is thus due to second-order effects. At 250 MHz, the predicted first-order pattern of a triplet methylene resonance and septuplet methine resonance is observed, giving both the chemical shift ( $\delta$ ) values and an accurate value of the coupling constant.

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The proton resonance spectra of norbornane<sup>6</sup> (1) and norbornene<sup>7</sup> (2) have also been analysed and



assigned and the complexities of the spectra overcome by polydeuteriation.<sup>7,8</sup> The spectrum of norbornane at higher applied fields is resolved sufficiently to obtain accurate values of the chemical shifts, but not enough for a full analysis. However, that of norbornene, with decoupling of the olefinic protons, is sufficiently well resolved to be analysed fully by computational methods. Marshall *et al.*<sup>8</sup> prepared the hexadeuterio derivatives in order to analyse the vicinal couplings of the eclipsed methylene groups in norbornenes and norbornanes, and theoretically explained their results. However, no complete analysis of the <sup>1</sup>H spectrum of norbornene has been given. Owing to the molecular symmetry, the spectrum is, with the olefinic protons decoupled, an AA'BB'MM'RX spin system which will always require detailed analysis at any field strength. As there is a lack of good coupling data for the parent hydrocarbon, this analysis was undertaken to give accurate values of all the NMR parameters.

## RESULTS AND DISCUSSION

### Molecular geometries

The molecular geometries of these molecules have been investigated in some detail. However, there remained some elements of uncertainty in these investigations which prompted the present calculations.

The geometry of adamantane follows from symmetry considerations, in the absence of a well defined experimental geometry. Dunitz<sup>9</sup> has given the symmetry imposed correlation between the methine and methylene CCC angles, i.e. if one increases from the tetrahedral angle the other must decrease. In consequence, following Fort and Schleyer,<sup>5</sup> we use the diamond structure with C—C and C—H bond lengths of 1.54 and 1.09 Å, respectively.

The structure of norbornane has been extensively investigated, the major aspects of interest being the presence of a number of very similar C—C bonds in the molecule which gives rise to problems in the interpretation of the experimental data, and the possible existence of steric repulsions between the *endo*-protons causing some distortion of the CCH angles. A recent combined electron diffraction and theoretical investigation<sup>10</sup> reported the carbon skeleton but not the hydrogen positions. These were

Table 1. Proton structural parameters for norbornane and norbornene<sup>a</sup>

	MNDO		<i>Ab initio</i>	
	Norbornane	Norbornene	Norbornane <sup>d</sup>	Norbornene <sup>e</sup>
<b>CCH Angles:</b>				
Bridge protons <sup>b</sup>	114.6	114.0	113.0	112.9
Bridgehead protons	115.4	117.8	116.1	120.1
<i>exo</i> -Protons <sup>c</sup>	111.7	111.3	110.8	111.4
<i>endo</i> -Protons <sup>c</sup>	113.5	112.1	112.0	111.5
HC=C	—	128.9	—	122.1
<b>HCH angles:</b>				
Bridge protons	105.6	105.8	109.7	109.3
<i>exo-endo</i>	106.1	106.0	108.0	107.5
<b>Torsional angles:</b>				
Bridge-bridgehead	61.0	60.8	62.6	64.4
Bridgehead- <i>exo</i>	41.6	43.0	42.3	43.6
Bridgehead- <i>endo</i>	78.3	75.8	78.3	74.2
<i>exo-endo</i>	118.4	118.5	120.9	119.9
Bridgehead-olefinic	—	19.9	—	19.8

<sup>a</sup> All C—H bonds were taken as 1.09 Å (saturated) and 1.08 Å (unsaturated).

<sup>b</sup> In norbornene CCH-*syn* = CCH-*anti*.

<sup>c</sup> C-1—C-6H equals C-5—C-6H (see 2).

<sup>d</sup> 4-21 G, Ref. 10;

<sup>e</sup> STO-3G.

obtained by both MNDO<sup>11</sup> and *ab initio*<sup>12</sup> calculations retaining the carbon skeleton of Ref. 10, and the results obtained are given in Table 1.

The geometry of norbornene has been reported by Chiang *et al.*,<sup>13</sup> based on a combined analysis of the microwave and electron diffraction data, neither technique on its own giving an unambiguous geometry. The final geometry was arrived at by making various assumptions, e.g. that all C—H bonds were equal. Thus, in order to obtain a well defined geometry including all the protons, a geometry optimization was performed in the same manner as that of norbornane, i.e. the carbon skeleton of Ref. 13 was used and the various CCH angles optimised using MNDO and *ab initio* (STO-3G) calculations. The MNDO optimizations were unconstrained, apart from maintaining the molecular symmetry, but in the *ab initio* case it was more convenient computationally to equalize all the *exo*-CCH angles and separately all the *endo*-CCH angles. These results are also given in Table 1.

Both calculations show that there is little change in the CH<sub>2</sub>CH<sub>2</sub> fragment in norbornane and norbornene. In principle there are two *exo*- (and two *endo*) CCH angles for each CH<sub>2</sub> group. However, the unconstrained MNDO calculation gave very similar values for these angles, i.e. the HCH plane is orthogonal to the CCC plane, as is the case for an unstrained methylene group. MNDO predicts a slight increase in the *endo*-CCH angles compared with the *exo*-CCH angles in norbornene and more so in norbornane. In the *ab initio* calculations this difference is much smaller in norbornane and zero in norbornene. Thus, any steric repulsion between the *endo*-protons in norbornane is not shown in the calculated geometry.

The calculated HCH angles are noteworthy. In the C-5—C-6 fragment and, also, more noticeably at the

bridge-carbon, the HCH angles are less than tetrahedral, even though the corresponding CCC angles are also much less than tetrahedral (C-5, 104.2; C-7, 95.3°). Hence the accepted view that the HCH angle in a methylene group increases when the CCC angle decreases does not appear to be supported by these calculations.

There is reasonable agreement between the MNDO and *ab initio* calculations but the latter show, in general, less distortion of the valency angles and these results will be used in our future calculations.

### NMR spectra

The 250 MHz <sup>1</sup>H spectrum of adamantane is first order and gives the vicinal coupling constant (3.30 ± 0.05 Hz) and chemical shifts immediately. The value of the coupling obtained is significantly different from previous estimates (1.7–2.6 Hz)<sup>5</sup> and in good agreement with predictions based on electronegativity rules (3.0 Hz).<sup>15</sup>

The 400 MHz <sup>1</sup>H spectrum of norbornane consists of two singlet peaks (with considerable fine structure), due to the bridge and bridgehead protons and a complex AB type pattern from the *exo*- and *endo*-protons. The patterns are all separate and give immediately the proton chemical shifts and the couplings to the bridge protons.

The bridge proton pattern was reproduced by means of a seven spin calculation with couplings of 1.8 Hz to the two bridgehead protons and an average coupling of 1.0 Hz to the four *endo*-protons, due to the two different couplings involved between the bridge and *endo*-protons. The analogous couplings in norbornene (see later) are 2.37 (7s, 6n) and ±0.25 (7a, 6n). These agree within the experimental error with the average coupling obtained above, provided *J*(7a, 6n) is negative. The complete norbornane spectrum is a 12 spin system, and was not analysed further.

In contrast to norbornane, the 250 MHz <sup>1</sup>H spectrum of norbornene with the olefinic protons decoupled was capable of a complete analysis. This was analysed as an eight spin system using both the PANIC<sup>16</sup> and NUMARIT<sup>17</sup> computer programs for spectral simulation. In practice, the PANIC program was found to be more convenient. In particular, the

capability of inputting the observed transition frequencies directly by peak spotting was a major asset in such a complex spectrum. Trial parameters for the spectral simulation were obtained from the literature<sup>4</sup> and the observed spectrum (note that the 7-*syn* and 7-*anti* signals are first-order patterns). The analysis proceeded smoothly, the final iteration being performed on 624 of the 980 calculated major transitions stored, producing an RMS error of 0.048 Hz. The results of this analysis are given in Table 2, and the observed versus calculated spectra shown in Fig. 1. The agreement is complete and the probable errors testify to a reasonably well determined analysis.

However, it is important to detail the ambiguities which arise in spectra of this symmetry. The AA'BB'MM'XR spectrum is invariant to the sign of *J*(AB) – *J*(AB'), *J*(AM) – *J*(AM') and *J*(BM) – *J*(BM'),<sup>18</sup> i.e. the pairs of couplings may be interchanged without affecting the spectrum. Further, in this weakly coupled spectrum the relative signs of the small couplings to the X and R nuclei are not well defined.

In practice, the only couplings which cannot be immediately differentiated on the basis of their expected values are *J*(1, 6n) and *J*(1, 5n); this will be considered further subsequently. The only small non-zero coupling involving the bridge protons is *J*(7a, 6n) which can be of either sign, but by analogy with the norbornane analysis is taken as negative.

The proton chemical shifts of the parent compounds are given in Table 3, together with the values obtained by previous investigations. Table 3 also includes the corresponding data for cyclohexane (in CCl<sub>4</sub> at –80 °C). The general agreement is very satisfactory and usually well within the quoted experimental errors of the previous investigations (*ca* ± 0.02 ppm). The large difference in the chemical shifts of cyclohexane compared with those in Ref. 22 is noteworthy and is due to the anisotropic CS<sub>2</sub> solvent used in Ref. 22.

The chemical shifts measured here are accurate to <0.005 ppm, which allows, given equal accuracy of measurement of the substituted compounds, SCS to be accurate to 0.01 ppm. These will be considered elsewhere.<sup>23</sup>

The coupling constants obtained here also agree very well with those obtained previously, with some

Table 2. Proton chemical shifts and coupling constants for norbornene<sup>a</sup>

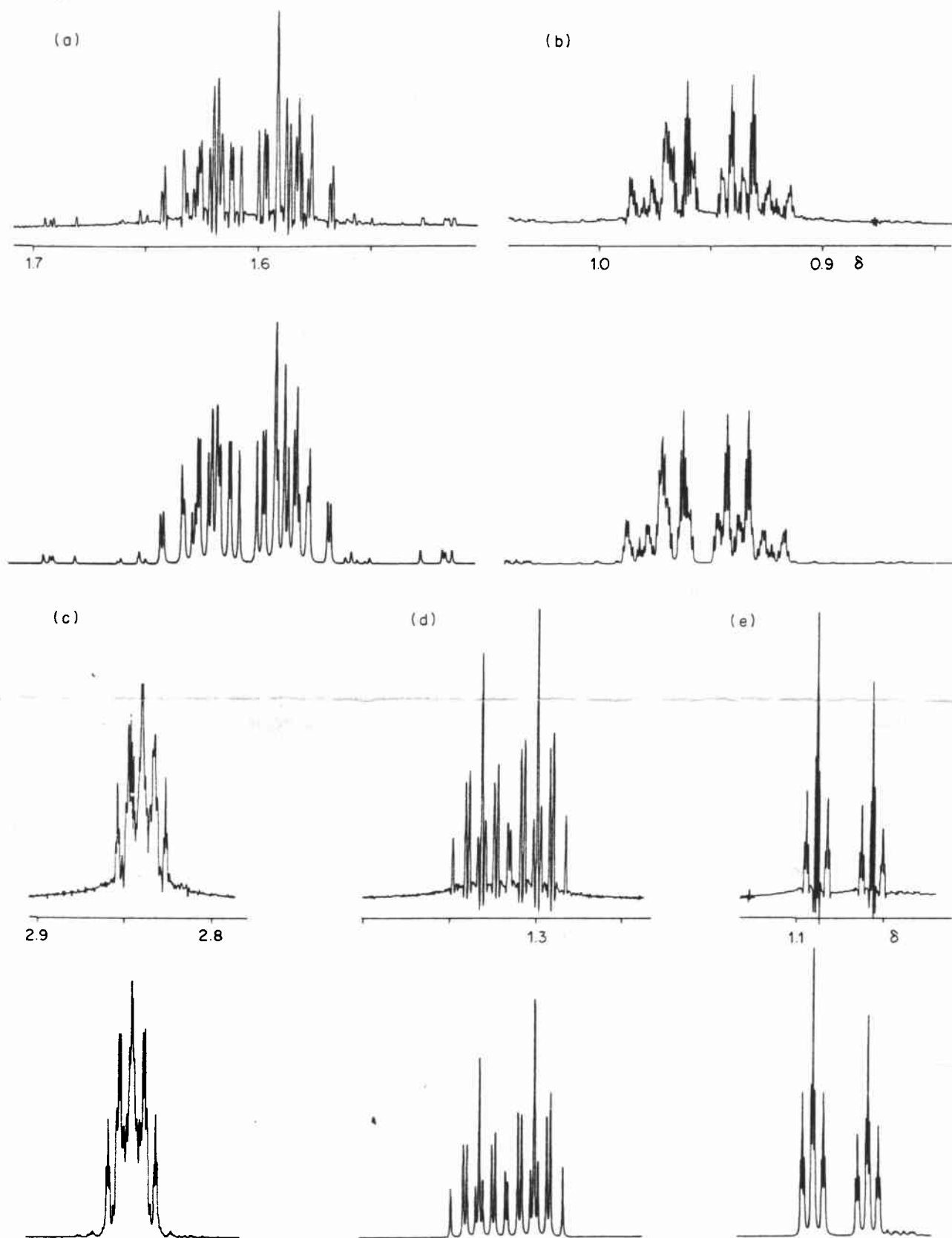
Chemical shift (Hz) <sup>b,c</sup>		Coupling constant (Hz) <sup>c</sup>			
H-1,4	710.59 (0.006)	<i>J</i> (14)	1.19 (0.014)	<i>J</i> (7s,6x)	0.00 (0.005)
H-5,6x	401.05 (0.003)	<i>J</i> (1,7s)	1.83 (0.006)	<i>J</i> (7s,6n)	2.37 (0.006)
H-5,6n	237.95 (0.006)	<i>J</i> (1,7a)	1.51 (0.006)	<i>J</i> (7a,6x)	0.00 (0.005)
H-7s	328.52 (0.005)	<i>J</i> (1,5x)	–0.15 (0.009)	<i>J</i> (7a,6n)	0.25 (0.006)
H-7a	268.49 (0.005)	<i>J</i> (1,6x)	3.66 (0.009)	<i>J</i> (5x,6x)	9.38 (0.007)
		<i>J</i> (1,6n)	0.55 (0.011)	<i>J</i> (5x,6n)	3.91 (0.007)
		<i>J</i> (1,5n)	–0.08 (0.011)	<i>J</i> (5x,5n)	–11.29 (0.007)
		<i>J</i> (7s,7a)	–8.03 (0.006)	<i>J</i> (5n,6n)	9.02 (0.011)

<sup>a</sup> 0.15 M CDCl<sub>3</sub> solution with the olefinic protons decoupled.

<sup>b</sup> At 250 MHz.

<sup>c</sup> Probable errors in parentheses.

<sup>1</sup>H NMR SPECTRA AND GEOMETRIES OF NORBORNENE, NORBORNANE, ADAMANTANE



**Figure 1.** Observed (upper) and calculated (lower) 250 MHz <sup>1</sup>H spectra of norbornene with the olefinic protons decoupled: (a) H-5,6-*exo*; (b) H-5,6-*endo*; (c) H-1,4; (d) H-7s; (e) H-7a.