Substituent Chemical Shifts in NMR

3†—Carbonitrile SCS in Rigid Molecules

Raymond J. Abraham* and Julie Fisher
School of Chemistry, University of Liverpool, Liverpool, L69 3BX, UK

The complete analysis of the ^{1}H NMR spectra of 2-norbornene carbonitrile (*exo* and *endo*), 2-norbornane carbonitrile (*exo* and *endo*) and 1-adamantane carbonitrile is reported, using high-field NMR and COSY and proton–carbon correlation experiments to assign the spectra. These data, together with a previous analysis of 1-octadeuteriocyclohexane carbonitrile, when combined with data for the parent hydrocarbons provide an extensive data set of substituent chemical shift (SCS) values for carbonitriles in molecules of accurately known geometry. The change in geometry on the introduction of a CN group was investigated using *ab initio* and MNDO methods, and found to be negligible for the carbon framework but significant around the C—N bond for the *endo* derivatives. A noteworthy feature is that the shielding of the 3x and 3n protons in the norbornane carbonitriles cannot be explained by the magnetic anisotropy of the CN bond.

KEY WORDS   Proton NMR   Carbonitrile SCS   Norbornene   Norbornane   Adamantane carbonitriles

INTRODUCTION

In Parts 1 and 2 of this series,[1] accurate chemical shift data for the parent molecules of interest in these studies, namely cyclohexane, adamantane, norbornane and norbornene, were obtained and subsequently utilized, together with the corresponding data for some bromo-substituted compounds, to obtain the substituent chemical shifts (SCS) for the bromosubstituent at every proton in the molecules.

The theoretical analysis of these SCS for the bromo substituents proved difficult, in that even with the extensive data set obtained, the multi-functional nature of these SCS, which may well include electronic, polar and anisotropic contributions, all of which are not well defined quantitatively, prevented an unambiguous conclusion being reached. It was felt that the analysis of these SCS would be more amenable to quantitative analysis with a substituent group with more pronounced polar and anisotropic effects, but with less electronic perturbation than the bromo substituent. Of the simple substituent groups with cylindrical symmetry, the carbonitrile group would appear to be ideal, having a large dipole moment, considerable magnetic anisotropy and a much smaller electronic (inductive) effect than the bromo substituent. Here we present the detailed analysis of 2-*exo*- and 2-*endo*-norbornane and -norbornene carbonitrile and 1-adamantane carbonitrile which, together with the previously reported[3] results for eq- and ax-cyclohexane carbonitrile, provide an extensive data set for the carbonitrile substituent.

* Author to whom correspondence should be addressed.
† For Parts 1 and 2, see Ref. 1.

The ^{1}H NMR spectra of both the 2-*exo*- and 2-*endo*-norbornene carbonitriles (1) have been analysed previously.[2]

In 1965, Davis and van Auken[2] reported the analysis of the 60 MHz ^{1}H NMR spectra of the *exo*- and *endo*-OH, -COOMe and -CN derivatives of norbornene, making chemical shift assignments on the basis of expected shift differences and observed splitting patterns. They discussed in detail how the chemical shifts are assigned in the *endo*-hydroxy isomer, but only briefly those for the carbonitrile isomers.

The ^{1}H NMR spectrum of 2-*endo*-hydroxynorbornene[2] at 60 MHz has the olefinic proton resonances well separated, permitting relative assignments of these peaks to be made on the basis of observed loss of coupling on saturation of the relevant bridgehead proton resonance. Proton H-6 is assigned to low field of H-5. This pattern of olefinic proton assignments (i.e. H-6 to low field of H-5) is reported for all the derivatives discussed, and both isomeric forms. However, as the OH_{exo}, $COOMe_{exo/endo}$ and $CN_{exo/endo}$ olefinic proton resonances overlap to some extent, the picture is not as clear as for the OH_{endo} derivative.

Davis and van Auken[2] noted an important feature when comparing chemical shifts for the 3x and 3n protons in the *exo*- and *endo*-OH and -COOMe derivatives with those for 3x and 3n in the carbonitrile isomers, namely that the eclipsed 3-proton (3x in *exo*, 3n in *endo*) is at higher field than the corresponding proton in the isomeric compound, a trend not shown for the OH and COOMe derivatives. They suggested that this observation is indicative of a 'positive diamagnetic anisotropy' associated with the CN bond, rather than a substituent electronegativity effect.

As the ^{1}H NMR spectra of both the norbornene

carbonitrile isomers are not well resolved at 60 MHz, we have recorded them at 250 MHz and include these data here.

Proton chemical shifts for the α- and β-protons of cyclohexane carbonitrile have been reported. Hofner et al.[3] analysed the low-temperature ^{1}H NMR spectrum of 2,2,3,3,4,4,5,5-octadeuteriocyclohexane carbonitrile, permitting the α- and β-proton chemical shifts to be measured in both the axial and equatorial conformers.

The ^{1}H NMR spectra of 2-exo- and 2-endo-Norbornane carbonitrile (2) and of 1-adamantane carbonitrile have not been recorded previously. We give the complete analysis of the 400 MHz ^{1}H NMR spectra of both the norbornane isomers and the 250 MHz ^{1}H NMR spectrum of 1-adamantane carbonitrile.

X = CN, Y = H exo
X = H, Y = CN endo
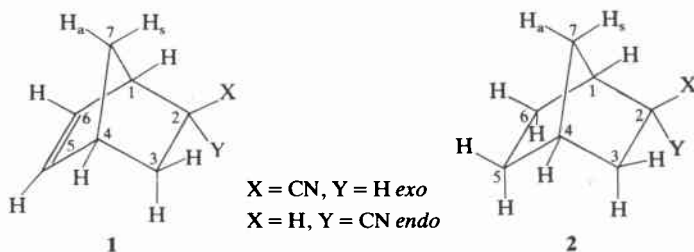
RESULTS

Exo- and endo-isomers of norbornene carbonitrile

The ^{1}H NMR spectra of the norbornene derivatives reported by Davis and van Auken[2] have many overlapping resonance patterns; therefore, we have recorded the 250 MHz spectrum of each isomer (see Tables 1 and 2) in order to confirm the assignments and chemical shift values reported.

The individual isomers were obtained[2] from preparative GLC of a mixture of the isomers; however, as there is very little difference in their physical properties, the simplest and most reliable method for identification of a particular isomer is consideration of its ^{1}H NMR spectrum and its relationship to that of the parent molecule, norbornene (3). Davis and van Auken[2] did not give the retention times (or state which isomer comes off the column first), which we could then have used for identification purposes. They noted that in the exo isomers the olefinic proton resonances are expected to be closer in chemical shift than in the corresponding endo isomer,[4] a point that their spectra confirm. Detailed analysis of the 250 MHz proton spectra allows an unambiguous identification of the isomers (see later).

Note that the IUPAC convention for numbering the bridge protons in norbornenes labels the proton syn to the C=C double bond as 7s; however, this convention causes confusion when comparing data obtained for the norbornenes with that for the norbornanes.

Therefore, we adopt the convention that 7s means this bridge proton is in a syn position to the substituent (anti to the C=C bond).

(a) Isomer 1 (shorter retention time on GLC column). The 250 MHz ^{1}H NMR spectrum of isomer 1 consists of six single proton resonances and a broad three proton resonance at ca 1.5 ppm. The bridgehead protons [on the basis of their broad resonance patterns which result from the many (small) coupling pathways available for protons in this position], the olefinic protons and the proton geminal to the substituent (whether it be an exo or endo proton, it will experience the greatest change on introduction of the 'CN' group, i.e. will have the largest SCS) are all readily assigned.

The result of a 2D COSY[5] experiment shows a correlation between the bridgehead proton at ca 3.0 ppm and a proton at ca 1.9 ppm, but no correlation with the proton geminal to the substituent. We can therefore assign this high-field bridgehead proton to H-4 and the proton at ca 1.9 ppm to H-3x. A correlation is also shown between H-4 and the '3-proton peak' and H-3x and the '3-proton peak,' hence we can assign H-7s/7a/3n [H-3x and H-3n are distinguished on the basis of their spin–spin couplings to the bridgehead proton H-4. As shown for norbornene[1a] $J(4, 3x)$ (ca 3.6 Hz) is much larger than $J(4, 3n)$ (ca 0.6 Hz).]

Further, as there is no correlation between H-1 and the proton geminal to the substituent, i.e. no significant coupling constant (although on saturation of the H-1 resonance the CHCN proton resonance sharpens), this unambiguously assigns the proton at ca 2.2 ppm to H-2n, and therefore this isomer (with the shorter retention time on the GLC column) is 2-exo-norbornene carbonitrile.

The olefinic protons are assigned on the basis of observed correlations between H-1 and the high-field olefin (H-6) and H-4 and the low-field olefin (H-5). These assignments are the reverse of those made by Davis and van Auken.[2] Figure 1 shows the ^{1}H NMR spectrum of this isomer.

(b) Isomer 2 (longer retention time, ENDO). The olefinic, bridgehead and 2-exo protons are readily assigned. A simple 2D COSY experiment shows that there are couplings between H-2x and the low-field bridgehead proton (which must therefore be H-1), and between the high-field bridgehead proton (H-4) and a proton with a chemical shift of ca 2.1 ppm, which must, therefore, be H-3x.

The olefinic protons are assigned again on the basis of their observed respective couplings to the bridgehead protons, H-5 to low field of H-6.

The 3n proton resonance assignment is confirmed on the basis of a large correlation with the 2x proton, and the 7s and 7a protons are distinguished by the observation of a correlation between 3n and the low-field bridge proton ('W' long-range coupling) which, therefore, permits assignment of 7a to low field of 7s.
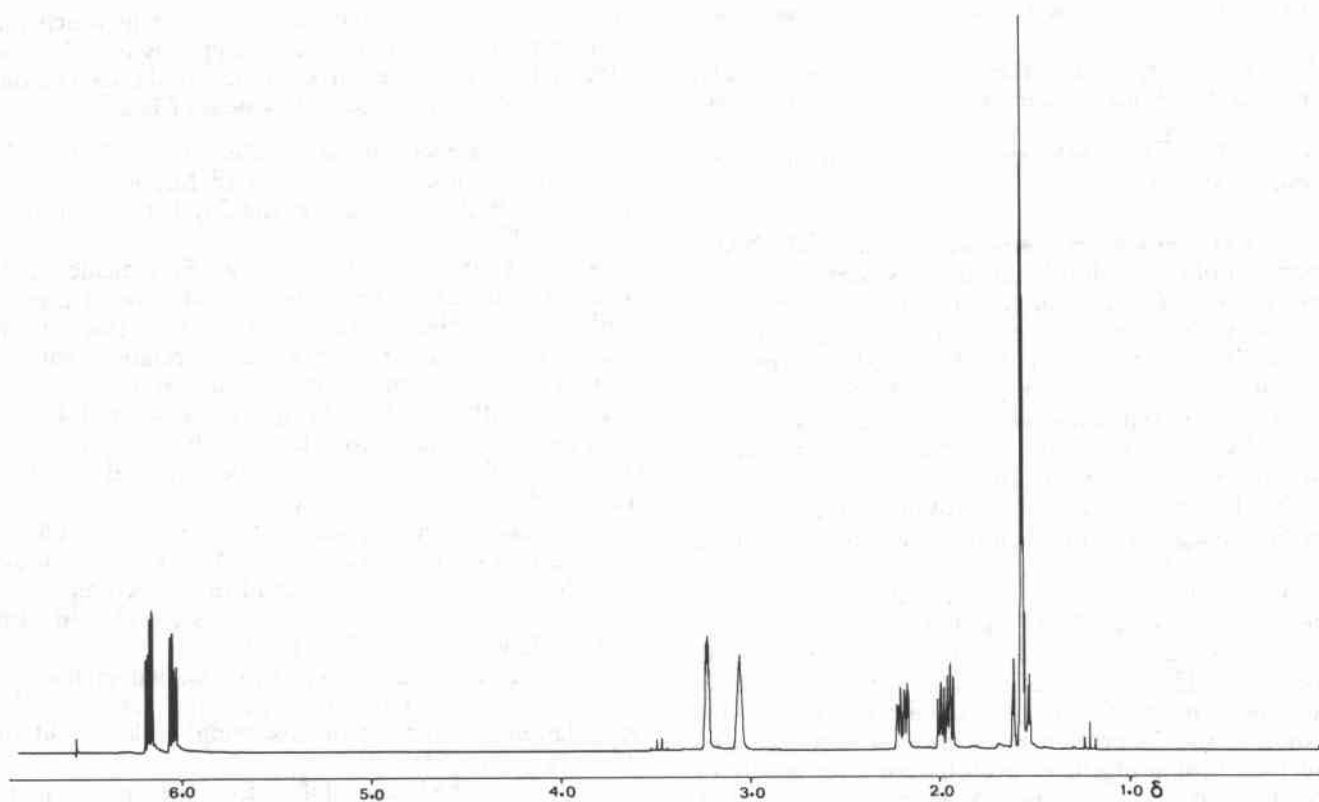
Figure 2 shows the ^{1}H NMR spectrum of isomer 2.

Figure 1. 250 MHz ¹H NMR spectrum of 2-*exo*-norbornene carbonitrile.

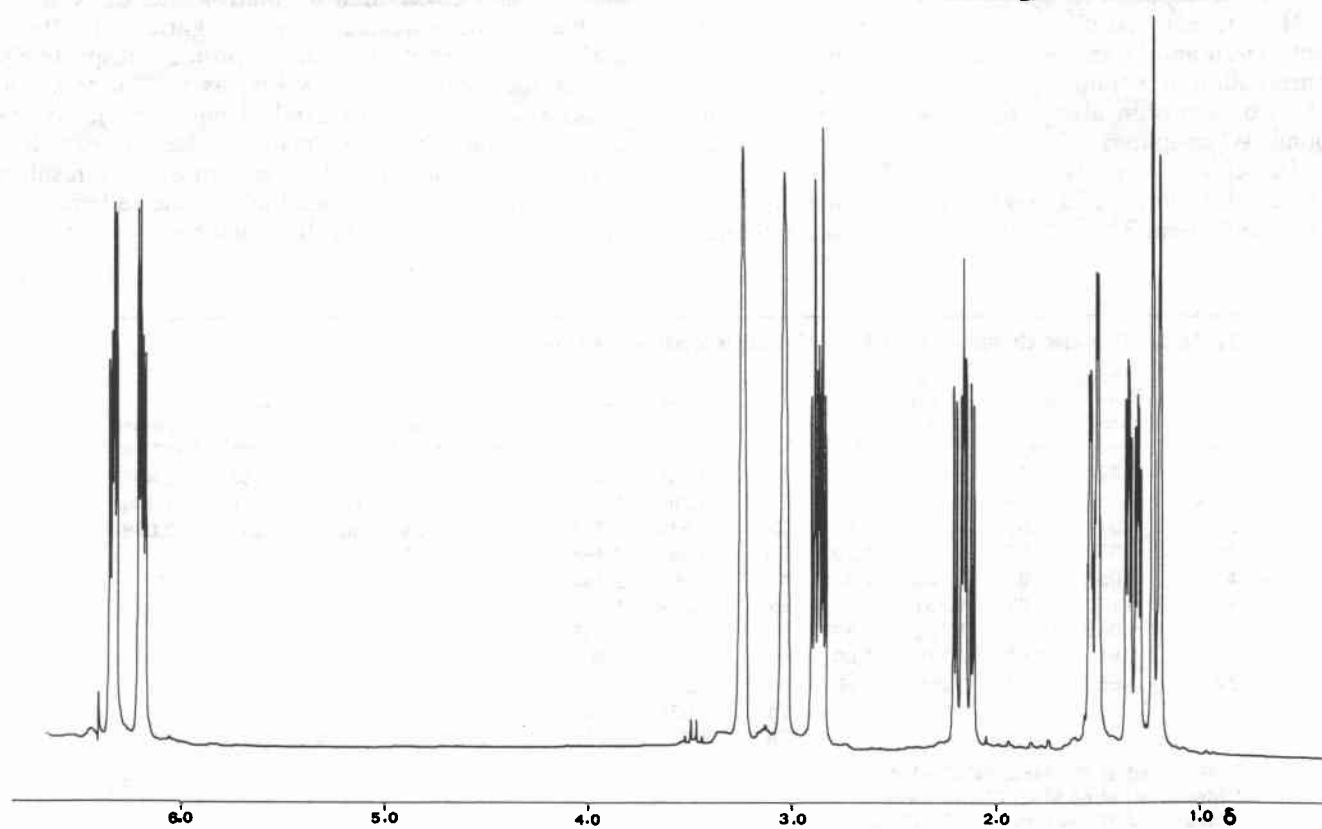**Figure 2.** 250 MHz ¹H NMR spectrum of 2-*endo*-norbornene carbonitrile.

EXO and ENDO isomers of norbornane carbonitrile

The ¹H NMR spectra of these isomers have not been reported but both isomers have been isolated[6] and their ¹³C spectra interpreted;[7] therefore, we only discuss their ¹H NMR spectra in detail (see also Tables 1 and 2).

(a) 2 EXO-norbornane carbonitrile. The ¹H NMR spectrum of this molecule, even at 400 MHz (Fig. 3) is very complex (an 11 spin system over a shift range of *ca* 2 ppm); however, with the aid of 1D homonuclear decoupling experiments and a 2D COSY experiment, all but two of the proton chemical shifts could be assigned. The remaining two were assigned following a ¹H/¹³C 2D correlation[8] experiment in which carbon–hydrogen connectivities are indicated.

The bridgehead and 2n proton resonances are readily assigned, and saturation at the resonance frequency of the high-field bridgehead proton results in the loss of a coupling of *ca* 3 Hz at *ca* 1.8 ppm. On the basis of 'expected' chemical shift differences (i.e. SCS values), this resonance can be assigned to H-3x as opposed to H-5x, and this assignment is confirmed by the observation of a large coupling of this (H-3x) proton to the 2n proton. Homonuclear decoupling of the high-field bridgehead proton spin also results in the loss of a significant coupling at *ca* 1.5 ppm [$J(4,5x)$], hence both H-4 and H-5x can be assigned unambiguously.

H-6x is assigned on the basis of a COSY experiment in which the low-field bridgehead proton (H-1) is seen to correlate with a proton at *ca* 1.6 ppm, which can only be H-6x (see Fig. 3).

H-3n is assigned on the basis of its correlation with both H-2n and H-3x. H-7a was assigned following the observation of a coupling of *ca* 2 Hz to both H-2n and H-3n of a proton absorbing at *ca* 1.4 ppm (the four bond 'W' coupling).

Therefore, H-1, H-4, H-2n, H-3x, H-3n, H-7s, H-6x, H-5x and H-7a have been assigned, but not H-6n and H-5n. The necessary information is obtained from the ¹H/¹³C correlation experiment in which the *endo* proton resonating at *ca* 1.2 ppm is found to be attached to the same carbon atom as the 6x proton. Hence, H-6n is assigned to low field of H-5n.

(b) 2-ENDO-norbornane carbonitrile. The 400 MHz ¹H NMR spectrum of this isomer is slightly less complex than that of the *exo* isomer, the 2x, 1 and 4 protons being well separated.

A 2D COSY experiment (Fig. 5) indicates that H-2x is coupled to the low-field bridgehead proton which must, therefore, be H-1 (and H-4 at *ca* 2.3 ppm). Proton H-4 shows a correlation with a proton at *ca* 1.9 ppm and another at *ca* 1.6 ppm, together with the two bridge protons at 1.4 and 1.3 ppm. H-2x also correlates with the proton at 1.9 ppm which can, therefore, be assigned to H-3x (and that at 1.6 ppm to H-5x).

Homonuclear decoupling of the H-3x spin results in the loss of a large coupling at *ca* 1.45 ppm, which must therefore be the chemical shift of the 3n proton.

H-6x is assigned on the basis of its correlation with the low-field bridgehead proton H-1.

H-6n and H-5n are assigned in a similar manner to those of the *exo* isomer (i.e. via their ¹H/¹³C correlations), H-6n again absorbing to low field of H-5n (see Figs 4 and 5).

The ¹³C chemical shifts for the norbornane derivatives are shown in Table 3.

1-Adamantane carbonitrile

The 250 MHz ¹H NMR spectrum of 1-adamantane carbonitrile gives only two separate proton resonances at δ 1.7 and 2.0 ppm, with relative intensities of 2:3 (Table 1). The assignments are straightforward, the β- and γ-protons (6 protons and 3 protons, respectively) having identical chemical shifts, as do the axial and equatorial δ-protons (3 axial, 3 equatorial). As was found for the 1-bromoadamantane derivative,[1b] there is very little structure to the resonances, as a result of the many pathways available in the adamantane system for long-range ¹H–¹H couplings.

Table 1. ¹H NMR chemical shifts for carbonitrile derivatives (ppm)

Proton	2-exo-Norbornene This work	Ref. 2[b]	2-endo-Norbornene This work[a]	Ref. 2[b]	Proton	2-exo-Norbornane[c]	2-endo-Norbornane[c]	Proton	1-Adamantane[a]	Proton	Axial cyclohexane[d]	Equatorial cyclohexane[d]
1	3.224	3.18	3.234	3.17	1	2.599	2.520	β	2.042	α	2.993	2.435
2n/x	2.187	2.18	2.858	2.85	2n/x	2.360	2.694	γ	2.042	ax	1.518	1.495
3x	1.977	1.92	2.148	2.10	3x	1.810	1.982	δe	1.735	eq	1.948	2.078
3n	1.560	1.50	1.318	1.20	3n	1.697	1.458	δa	1.735			
4	3.054	3.02	3.028	2.97	4	2.397	2.348					
5	6.169	6.03	6.331	6.15	5x	1.528	1.619					
6	6.045	6.20	6.189	6.30	5n	1.171	1.356					
7a	1.56	1.43	1.510	1.40	6x	1.570	1.505					
7s	1.56	1.50	1.205	1.20	6n	1.225	1.814					
					7s	1.621	1.308					
					7a	1.381	1.417					

[a] Measured at 250 MHz, CDCl₃–TMS.
[b] Measured at 60 MHz, CDCl₃–TMS.
[c] Measured at 400 MHz, CDCl₃–TMS.
[d] Ref. 3.

Table 2. ^{1}H–^{1}H Coupling constants for (a) 2-*exo*- and (b) 2-*endo*-norbornene carbonitrile[a] and (c) 2-*exo* and (d) 2-*endo* norbornane carbonitrile

(a)	1	2n	3x	3n	4	5	6	7a	7s
1	—								
	b								
2n	(0)	—							
		4.5							
3x	b	(4.2)	—						
		7.5[c]	12.4						
3n	b	(4.5)	(12.5)	—					
			3.4	b					
4	(0)	b	(3.4)	(0)	—				
	b	b	b	b	(3.0)	—			
5	3.0	0.4				5.7			
	(2.7)	(b)	b	b	b	(5.8)	—		
6	b			b	b				
	(1.8)	(3.0)	b	(3.0)	(1.8)	b	b	—	
7a				b		0.7	0.4		
	(1.4)	b	b	b	(1.4)	(0.8)	(0.8)	b	—
7s									

(b)	1	2x	3x	3n	4	5	6	7a	7s
1	—								
2x	(3.5)	—							
		9.4							
2x	b	(9.1)	—						
		3.8	−11.8						
3n	b	(3.4)	(11.5)	—					
		3.5	b						
4	(0)	b	(3.6)	(0)	—				
					2.0				
5	b	b	b	b	(2.6)	—			
	2.8					5.7			
6	(2.9)	b	b	b	b	(5.6)	—		
	b			2.4	1.8				
7a	(1.9)	b	b	(3.1)	(1.9)	b	b	—	
	b			b		b	b	−8.5	
7s	(1.3)	b	b	b	(1.3)	(0.4)	(0.4)	(8.6)	—

(c) J	Coupling (Hz)	(d) J	Coupling (Hz)
2n–3x	4.9	1–2x	4.1
2n–7a	1.6	1–7s	1.6
3x–3n	−12.6	1–7a	1.7
3x–4	2.7	2x–3x	11.9
3x–5x	1.5	2x–3n	4.9
3n–7a	2.4	2x–6x	2.1
4–7a	1.6	3x–3n	−12.5
1–7a	1.6	3x–4	4.4
7s–7a	−10.4	3x–5x	2.9
		3n–7a	2.4
		4–7a	1.7
		4–7s	1.6
		5x–6x	12.4
		5n–6x	4.1
		5n–7s	2.3
		6x–6n	−12.4
		6n–7s	2.2
		7s–7a	−10.0

[a] Figures in parentheses from Ref. 2.
[b] Coupling not resolved.
[c] J ± 0.5 Hz.

Geometry optimization calculations

The results of the geometry optimization calculations, performed for both the norbornane and norbornene derivatives using the MNDO[9] and GAUSSIAN 76[10] programs, show that there is very little change in the carbon frameworks compared with the starting geometries of the parent molecules.

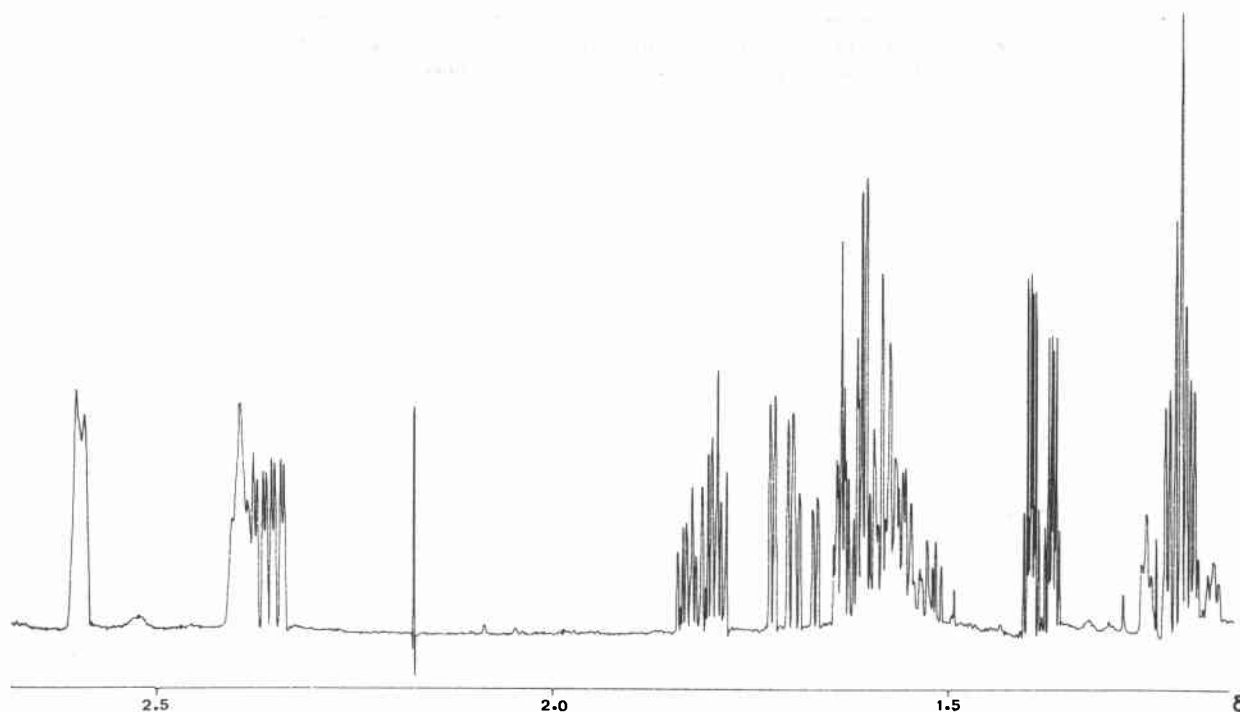There are significant angle changes around the substituent, which are larger in the MNDO than the

Figure 3. 400 MHz ¹H NMR spectrum of 2-*exo*-norbornane carbonitrile.

GAUSSIAN 76 calculations. Both the *exo* compounds give identical geometries with C—C—CN bond angles of 111.7° (GAUSSIAN 76), i.e. the same as the C—H bond which the substituent replaces, and 113.6° (MNDO). For the *endo*-norbornene carbonitrile this angle opens to 112.7° (114.7°), and for the *endo*-norbornane carbonitrile there is a further increase to 113.6° (116.2°). The HC—C angles are unaffected at *ca* 110.6° (GAUSSIAN 76) and 108–110° (MNDO). Hence the calculations indicate that there is some repulsive interaction, particularly in the *endo*-norbornane, presumably with the 6-*endo* proton.

All bond lengths are predicted well, including the C—C(N) and C≡N bond lengths of 1.46 and 1.16 Å,

respectively, in good agreement with experimental data.[11]

DISCUSSION

The SCS data for the carbonitrile substituent, derived from the results described here and those for the parent molecules,[1a] are presented in Table 4.

The data in Table 4 show a good consistency in that the SCS values in the norbornane and norbornene derivatives, for protons in similar orientations with respect to the substituent, are very similar. For
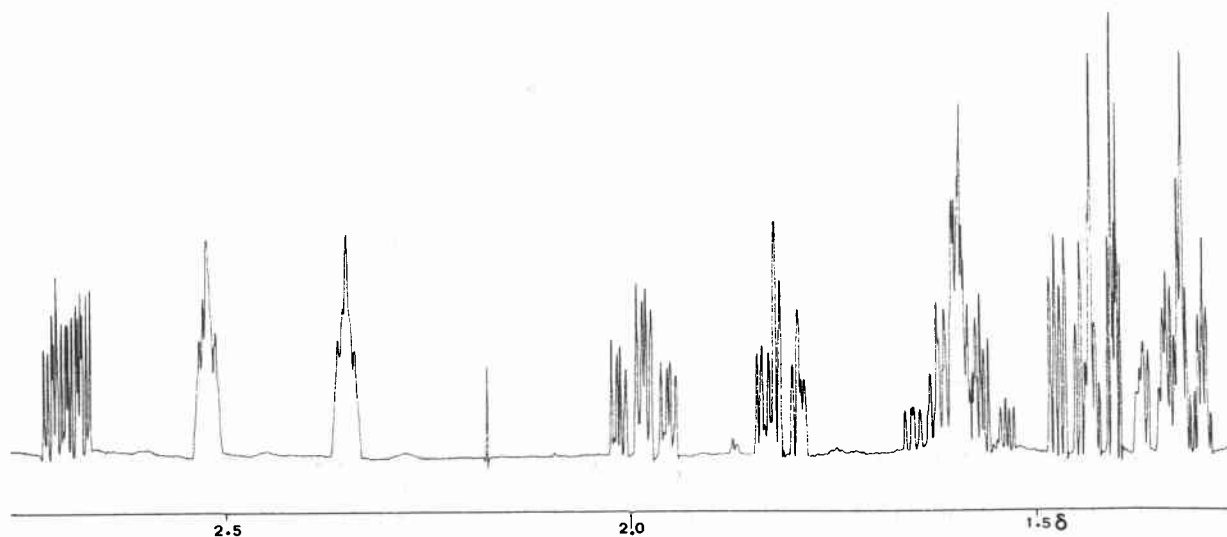
Figure 4. 400 MHz ¹H NMR spectrum of 2-*endo*-norbornane carbonitrile.
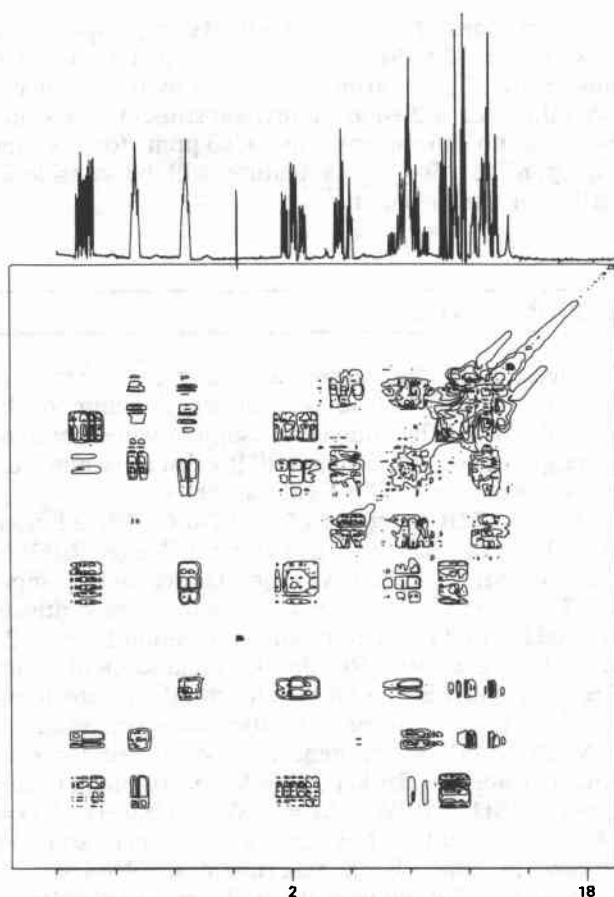
Figure 5. 250 MHz 2D COSY spectrum of 2-*endo*-norbornane carbonitrile.

example, the SCS for 7s in *exo*-norbornene carbonitrile is 0.48 ppm and that for the same proton in *exo*-norbornane carbonitrile is 0.44 ppm. Another example is afforded by the SCS of H-1 in the *exo*-norbornane and -norbornene derivatives, being 0.4 and 0.38 ppm, respectively.

This is pleasing because (as shown in Part 1[1a]) the geometry of the parent molecules is very similar and, as we have shown with the geometry optimization calculations, so are the geometries of the substituted molecules.

The geometry optimization calculations indicate that although there are no significant changes in the carbon frameworks, the position which the CN group occupies is slightly shifted from that of the proton it displaces. This 'shift' is most significant in the 2-*endo*-norbornane carbonitrile derivative in which the CN—C-2—C-1 (see **2**) angle increases, moving the CN group away from the 6n proton.

Because of the similarities noted in the SCS values and molecular geometries, in calculations to be reported at a later date[12] we use the geometries of the norbornane system and 'average' SCS values as shown in Table 5.

As mentioned, the calculations suggest little geometry change in the remainder of the molecule, and this is reinforced by the similarity shown in the coupling constants reported here and those for norbornene[1a] and 2-*exo*-bromonorbornane.[1b] For example, in 2-*exo*-bromonorbornane[1b] $J(7a, 3n) = 2.4$ Hz, $J(7a, 4) = 1.7$ Hz, $J(7a, 7s) = -10.0$ Hz, $J(6x, 5n) = 3.8$ Hz and $J(6x, 6n) = -12.6$ Hz; these

Table 3. ^{13}C NMR chemical shifts for norbornane carbonitriles (ppm)

	2-*endo*-Norbornane carbonitrile			2-*exo*-Norbornane carbonitrile	
Carbon	This work[a]	Ref. 7[b]	Carbon	This work[a]	Ref. 7[b]
1	39.86	39.7	1	41.82	41.8
2	30.07	29.7	2	31.03	30.6
3	35.38	35.1	3	36.09	35.9
4	36.53	36.5	4	36.04	36.0
5	29.07	28.9	5	28.36	28.1
6	24.93	24.7	6	28.47	28.0
7	38.72	38.2	7	37.18	36.9

[a] $CDCl_3$–TMS, recorded using a Bruker 400 WM spectrometer.
[b] δ Values upfield to CS_2, converted to the TMS scale $(-\delta = \delta_{TMS} - \delta_{CS_2})$.

Table 4. Substituent chemical shifts for CN compounds (ppm) $(\delta_{CN} - \delta_H)$

	Norbornene carbonitrile			Norbornane carbonitrile			Adamantane		Cyclohexane	
Proton	exo	endo	Proton[b]	exo	endo	Proton	carbonitrile	Proton[c]	Axial	Equatorial
1	0.383	0.393	1	0.407	0.328	β	0.289	1 eq/ax	1.314	1.247
2n/x	1.236	1.255	2n/x	1.198	1.223	γ	0.168	2 ax	0.330	0.307
3x	0.374	0.545	3x	0.399	0.511	δe	−0.018	2 eq	0.269	0.399
3n	0.609	0.367	3n	0.535	0.296	δa	−0.018			
4	0.213	0.187	4	0.205	0.156					
5	0.184	0.346	5x	0.057	0.148					
6	0.060	0.204	5n	0.009	0.194					
7a	0.247	0.197	6x	0.099	0.094					
7s	0.487	0.132	6n	0.063	0.652					
			7s	0.440	0.127					
			7a	0.200	0.236					

[a] Recorded at 250 MHz.
[b] Recorded at 400 MHz.
[c] Ref. 3.

Table 5. Average SCS values for norbornane/norbornene carbonitriles

Proton	exo SCS (ppm)	Proton	endo SCS (ppm)
1	0.395	1	0.360
3x	0.356	3x	0.528
3n	0.572	3n	0.331
4	0.209	4	0.171
5x	0.057	5x	0.148
5n	0.009	5n	0.194
6x	0.099	6x	0.094
6n	0.063	6n	0.652
7s	0.463	7s	0.129
7a	0.233	7a	0.216

values are virtually identical with the corresponding couplings in both the exo- and endo-norbornane derivatives.

In the norbornene derivatives, if we consider the parent molecule norbornene,[1a] we find $J(1, 2x) = 3.6$ Hz, $J(3x, 2n) = 3.9$ Hz and the 'geminal' exo-[1]H–endo-^{1}H coupling constant is -11.3 Hz. These data are, again, virtually identical with those for the exo- and endo-carbonitrile derivatives of norbornene.

The results in Table 2 show disagreement in the $J(3n, 2n)$ value reported by us and by Davis and van Auken[2] for the exo isomer. However, our value is unambiguous and in good agreement with the corresponding coupling measured in the parent molecule. The remaining data which we have obtained for the norbornene carbonitriles compare well with those in Ref. 2; there is, however, one discrepancy which arises in the analysis of both isomeric compounds, namely, the assignments of the olefinic protons. As mentioned, the 60 MHz spectra of 2-exo- and 2-endo-norbornene carbonitrile show overlapping olefinic proton resonances; however, as shown in Figs 1 and 2, at 250 MHz the olefinic proton resonances of both isomers are well separated, permitting assignments to be made unambiguously from the 2D COSY experiments.

The chemical shift differences (SCS values) show similar trends to those reported in Part 2,[1b] but one particular trend is worth noting.. As was found for 2-exo-bromonorbornane,[1b] the 3x proton of the 2-exo-norbornane/norbornene derivatives is deshielded to a lesser extent than the 3n proton (a similar pattern is observed for the 2-endo-carbonitriles, i.e. 3n is deshielded to a lesser extent than 3x). As we shall discuss at greater length in a subsequent paper, none of the current theories on SCS calculations can predict such an observation. This trend was noted by Davis and van Auken[2] for the norbornene derivatives, which they suggested could be explained by the 'positive diamagnetic anisotropy of the CN bond.' However, our calculations suggest that this may not be the answer.

Using the value of $\Delta\chi(C\equiv N)$ obtained by Flygare[13] of -13.5×10^{-6} cm^3 mol^{-1} with the above geometries gives a *deshielding* for the 6n proton in the 'endo' series of $+0.26$ ppm, but a *shielding* for both the 3x

and 3n protons of -0.18 and -0.08 ppm, respectively; thus, the 3x–3n discrepancy is not due to the CN anisotropy. This is further supported by the analogous $\Delta\delta$ values for a 2-endo-methyl substituent, for which there is no anisotropy, of $+0.3$ ppm for 3x and -0.6 ppm for 3n.[14] This feature will be considered further in a later paper.[12]

EXPERIMENTAL

A mixture of the 2-exo and 2-endo isomers of norbornene carbonitrile was obtained commercially from Aldrich. The individual isomers were obtained by preparative GLC using a 10 ft column (6 mm i.d.) of 10% Reoplex 100 on Celite at 200 °C.
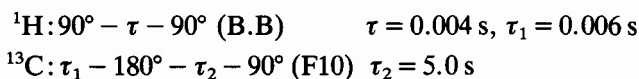
The ^{1}H NMR spectrum of ca 0.1 M CDCl$_3$ solutions of each isomer was recorded using a Bruker 250 WM spectrometer equipped with an Aspect 2000 computer. The spectral parameters included sweep widths of ca 1900 Hz in 8 K memory and acquisition time ca 2 s over 32 transients. Resolution enhancement using GB = 0.4 and LB = -0.8 was followed by zero filling into 32 K memory prior to Fourier transformation.

A 2D COSY experiment was performed for each isomer (using the Bruker 250 WM spectrometer) using SI = 1 K, SI1 = 512W, SW = 2SW1 = 1500 Hz, YD = 1 K, TD1 = 128W = NE and a 'sine bell squared' window function. Each experiment involved sixteen scans and two dummy scans with an initial delay of 5 s. The pulse sequence consisted of two 90° pulses.

The 2-exo- and 2-endo-norbornane carbonitrile isomers were prepared from the corresponding norbornene by reduction of the carbon—carbon double bond using a palladium–charcoal catalyst in an aromatic solvent–sodium phosphate–water system.[15]

The ^{1}H NMR spectrum of ca 0.1 M CDCl$_3$ solutions of each isomer was recorded using a Bruker 400 WM spectrometer. Spectral parameters included sweep widths of ca 1200 Hz in 16 K memory and zero filling into 32 K following resolution enhancement using GB = 0.3 (0.4), LB = -0.5 (-0.35) (the figures given in parentheses refer to the exo isomer).

The ^{1}H/^{13}C correlation experiment was performed on a mixture of the exo- and endo-norbornane carbonitrile isomers using the XHCORR.AU microprogram, available as part of the Bruker software for the Aspect 2000 computer system. The pulse sequence is as follows:

$$^1\text{H}: 90° - \tau - 90° \text{ (B.B)} \qquad \tau = 0.004 \text{ s}, \tau_1 = 0.006 \text{ s}$$

$$^{13}\text{C}: \tau_1 - 180° - \tau_2 - 90° \text{ (F10)} \qquad \tau_2 = 5.0 \text{ s}$$

The experiment was performed using the Bruker 400 WM spectrometer using a 1.8 M CDCl$_3$ solution plus ca 1% TMS with SW1 (^{1}H) = 620 Hz, SW (^{13}C) = 2500 Hz, TD = 2 K, SI = 2 K, TD1 = 232 W, SI1 = 512W and NE = 232. Proton spin decoupling was achieved using a decoupler power of 12H, and a 'sine bell squared' window function was used for the 2D Fourier transformation. A 2D COSY experiment was performed for each isomer using SW = 2SW1 = 800 Hz, SI = 2SI1 = 1K, TD = 1K and TD1 = 128W,

NE = 128, NS = 16, DS = 2 for the *endo* isomer, and SW = 2SW1 = 760 Hz, SI = 2SI1 = 1K, TD = 1K, TD1 = NE = 128W, NS = 64, DS = 2 for the *exo* isomer. An initial delay of 5 s before the $90°–\tau–90°$ ($\tau = 3 \times 10^{-6}$ s) pulse sequence was used in both experiments. Fourier transformation in each case was performed using a 'sine bell squared' window function.

The ^{1}H NMR spectrum of 1-adamantane carbonitrile, obtained from Aldrich, was recorded using SW = 815 Hz and an acquisition time of 5 s, in 8 K zero filling into 32 K following the use of resolution enhancement factors of LB = −0.5 and GB = 0.3, on a Bruker 250 WM spectrometer.

The geometry optimization calculations for the *exo*- and *endo*-norbornane and -norbornene derivatives were performed using the MNDO[10] program and starting geometries described in Part 1.[1a] A C—C(N)

bond length of 1.54 Å and a C≡N bond length of 1.16 Å were used. All bond and torsional angles were allowed to change, as were all bond lengths apart from those of the C—H bonds (a 1.09 Å bond length is used).

REFERENCES

1. (a) R. J. Abraham and J. Fisher, *Magn. Reson. Chem.* **23**, 856 (1985); (b) R. J. Abraham and J. Fisher, *Magn. Reson. Chem.* **23**, 862 (1985).
2. J. C. Davis and T. V. van Auken, *J. Am. Chem. Soc.* **87**, 3900 (1965).
3. D. Hofner, S. A. Lesko and G. Binsch, *Org. Magn. Reson.* **11**, 179 (1978).
4. R. J. Ouellete and G. E. Booth, *J. Org. Chem.* **30**, 423 (1965).
5. W. P. Aue, E. Bartholdi and R. R. Ernst, *J. Chem. Phys.* **64**, 2229 (1976).
6. P. Wilder, Jr, and D. B. Knight, *J. Org. Chem.* **30**, 3078 (1965).
7. J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith and J. D. Roberts, *J. Am. Chem. Soc.* **92**, 7107 (1970).
8. A. Bax and G. A. Morris, *J. Magn. Reson.* **42**, 501 (1981).
9. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4889, 4907 (1977).
10. J. A. Pople, J. S. Binkley, R. A. Whiteside, P. C. Hariharam, R. Seeger, W. J. Hehre and N. D. Newton, *GAUSSIAN 76*, QCPE program No. 368, Vol. 11 (1978).
11. K. H. Hellwege and A. W. Hellwege (Eds), *Landolt–Börnstein, Volume 7, Structure Data of Free Polyatomic Molecules*, p. 177. Springer-Verlag, Berlin (1976).
12. R. J. Abraham and J. Fisher, manuscript in preparation.
13. W. H. Flygare, *Chem. Rev.* **74**, 663 (1974).
14. E. Pretsch, H. Immer, C. Pascual, K. Schaffner and W. Simon, *Helv. Chim. Acta* **50**, 105 (1967).
15. P. J. Price, personal communication.