Substituent Chemical Shifts in NMR

2*—Bromine SCS in Rigid Molecules

Raymond J. Abraham† and Julie Fisher
School of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

The complete analysis and assignment of the ^{1}H NMR spectra of 2-*exo*-bromonorbornane (1) and 2-bromoadamantane is reported, using high-field NMR and COSY and proton–carbon correlation experiments to assign the spectra. These data, together with those for the parent hydrocarbons, when combined with previous analyses of 1-bromoadamantane, 1-bromooctadeuterocyclohexane and the simple alkyl bromides, provide a data set of 38 proton SCS values for bromine in molecules of accurately known geometry. The effect of solvent on the SCS was investigated for 1 in five common solvents of very different polarity (C_6D_{12} to DMSO). Only small (< 0.1 ppm) solvent shifts were observed, apart from the 2-*endo* and 7*s* protons. A noteworthy feature of the SCS is the downfield shift of the CHX proton in all the series investigated, as X changes from Cl to Br to I. This is the reverse of the 'normal' trend and cannot be explained by present theories of SCS.

INTRODUCTION

The calculation and prediction of proton substituent chemical shifts (SCS) has been of interest for many years.[2] As early as the 1950s Dailey and Shoolery[3a] and Allred and Rochow[3b] were attempting to correlate data obtained for monosubstituted methanes and ethanes with substituent electronegativity. In doing so they noted that there was an almost linear relationship between chemical shifts for the methanes and the difference in shifts [δ(internal)] between the methyl and methylene protons of the ethanes. Moreover, both of these quantities were found to be linearly related to the electronegativity of the substituent in question, hence suggesting a method by which other substituent electronegativities may be measured.

However, some anomalies arose in their treatment, particularly when considering α-protons in isopropyl halides (Cl, Br, I). Subsequent investigations[2] showed that the SCS for bicyclic compounds such as bicyclo[2.2.1]heptene derivatives were very 'stereochemistry' dependent, and could not be explained solely by the inductive effect of a substituent.

It has since been suggested[4] that the success of the Dailey and Shoolery relationship was due to the fortuitous cancellation of various 'long-range' effects at the α and β positions. These 'long-range' effects may be the result of the involvement of the C – X (X being the substituent) bond electric dipole moment, magnetic anisotropy, Van der Waals interactions or changes in solute–solvent interactions, all of which must be considered in order to provide a general method for the calculation of the SCS. Zurcher[5] studied the contributions of each of these factors in an authoritative review of this problem. As Shoolery and Dailey were limited to using data for α- and β-protons in alkyl groups, Zurcher was limited to using data available for methyl groups in various steroid and bornane derivatives.

Many of the problems encountered in these early investigations have been caused by the lack of a set of SCS values for a series of protons in different, but precisely known, orientations from the substituent. Such a data set would enable all possible contributions, stereochemical or otherwise, to be investigated. Modern experimental NMR techniques make this a feasible proposition, and we present here such a data set for a common substituent, namely bromine. The detailed theoretical treatment of these data will be presented later.

To minimize the possibility of errors being brought into our calculations, we chose to study molecules with well defined geometries, in particular adamantane, norbornane and cyclohexane derivatives.[1]

The analyses of the ^{1}H NMR spectra of 1- and 2-bromoadamantane and axial and equatorial bromocyclohexane have been reported;[6–8] however, there has been no reference to the ^{1}H NMR spectrum of 2-*exo*-bromonorbornane, which is hardly surprising when (as discussed later) we consider the complexity of its NMR spectrum, even at 400 MHz.

The ^{1}H NMR spectrum of 2,2,3,3,4,4,5,5-bromocyclohexane-d_8 (**4**) has been analysed by Hofner *et al.*[8] They studied various 1-substituted d_8-cyclohexanes by low-temperature NMR spectroscopy, allowing the ^{1}H chemical shifts of the 1- and 6-axial and 6-equatorial protons to be measured in both the axial and equatorial conformers. The values they obtained (and which we have checked using the non-deuteriated cyclohexane) for the axial and equatorial bromocyclohexane are included here.

In 1965 Fort and Schleyer[6] reported the ^{1}H NMR spectra of adamantane and several of its 1-substituted derivatives (**3**). The spectra of these molecules are relatively simple, generally showing only three proton

* For Part 1, see Ref. 1.
† Author to whom correspondence should be addressed.

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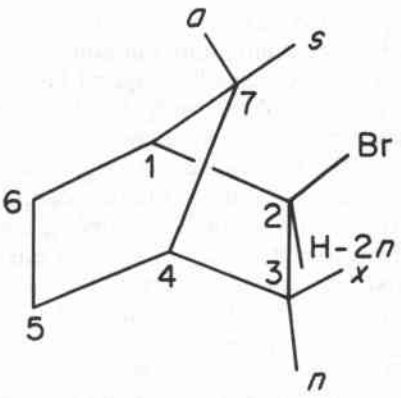

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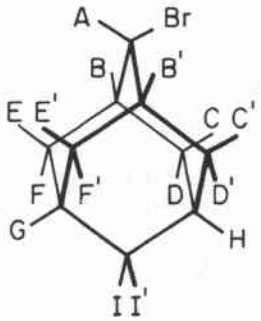

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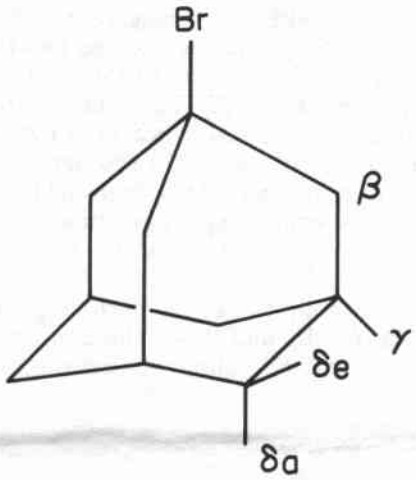

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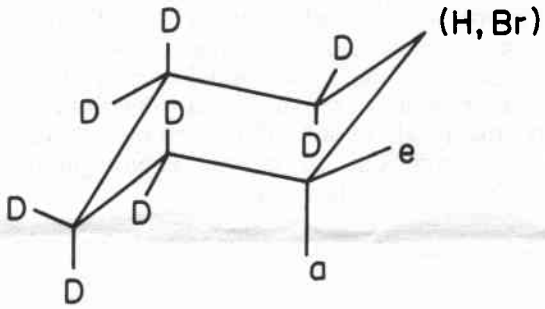

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resonances, β, γ and δ (δ_e and δ_a being accidentally equivalent) and a feature of such highly symmetric molecules was a 'precise chemical shift additivity relationship.'[6] In an attempt to rationalize the observed substituent chemical shifts, Fort and Schleyer found that virtually any measure of substituent electronegativity correlated well with the shifts they had measured. They also drew attention to an interesting trend in δ values for the halogen derivatives. The β-proton of 1-fluoroadamantane resonates to high field of the corresponding proton in the chloro, bromo and iodo derivatives. This trend reversed, and then reversed again, for the γ- and δ-protons, respectively. This pattern, Fort and Schleyer concluded, could only be explained by the involvement of the C—X (X = halogen) bond magnetic anisotropy in determining the chemical shift, because electrostatic factors alone would not produce such a result. However, other workers[9,10] have stated that for halogen-substituted compounds the C—X bond anisotropy is of minimal importance in determining SCS values.

Van Deursen and co-workers[7] reported the results of an extensive study of 2-substituted and 2,4-disubstituted adamantanes. In their initial report[7a] they analysed the ^{1}H NMR spectra of OH, Cl, Br, I and NH_2 2-substituted adamantanes, making chemical shift assignments on the basis of 'expected' chemical shift differences and consideration of structural features. For example, protons C–D of **2** are distinguished on the basis that C experiences a 1,3-diaxial interaction with the substituent which is deshielding, hence the low-field doublet must be assigned to C. They reported chemical shift values for protons A, B, C, D and I, but, because of the limitations of the low-field instrument used (Varian HA 100), the shift values for E, F, G and H appeared to be equivalent. In a later study involving analysis by the use of INDOR[7b,c] of disubstituted adamantanes, Van Deursen and co-workers estimated the chemical shifts for E and F, placing E to high field of F.

Since the ^{1}H NMR spectrum of 2 bromoadamantane at 100 Mz is only partially resolved, we recorded the spectrum at 400 MHz in an attempt to clarify and confirm the chemical shift assignments made by Van Deursen and co-workers. This analysis, together with that of 2-*exo*-bromonorbornane, is discussed below.

RESULTS AND DISCUSSION

2-*exo*-Bromonorbornane

The ^{1}H NMR spectrum of 2-*exo*-bromonorbornane (**1**) at 400 MHz is virtually first order in appearance (Fig. 1), the complexity of the splitting patterns clearly indicating the many paths available in this rigid cyclic system for normal and long-range spin–spin coupling.[11]

The spectrum consists of 10 separate resonance patterns (this is an 11 spin system, but two protons have almost equivalent chemical shifts). The lowest field pattern at *ca* δ 4.0 is obviously assigned to the 2*n* (C*H*Br) proton, and the resonances at *ca* δ 2.5 and 2.3 can be assigned to the bridgehead protons 1 and 4 (although we have not, as yet, determined the order). There is very little structure in these resonances, as would be predicted for these positions where there are possibilities for spin–spin couplings to six or seven other protons, all of which are relatively small in size and not distinguishable. (These broad peaks are characteristic of bridgehead protons in all unsymmetrical norbornane and norbornene derivatives.) Although many simple one-dimensional homonuclear decoupling experiments were performed to clarify the assignments, the result of a COSY two-dimensional experiment[12] is sufficient to permit unambiguous assignment of all but two chemical shifts.

Figure 2 shows the result of a COSY two-dimensional experiment, and our analysis proceeded as follows. We have already assigned H-2*n* and made relative assignments of the bridgehead proton shifts. If we first consider correlations between H-2*n* and other protons, it is seen that there is a large coupling to the two protons at *ca* δ 2.0, a smaller coupling to the proton at δ 1.3 and a smaller coupling again to the bridgehead proton at *ca* δ 2.5. On the basis of these observations, and consideration of the orientation of 2*n* with respect to the other protons in the molecule, we can assign the peak at *ca* δ 2.0 to the 3*x*/3*n* protons, the peak at δ 1.3 to 7*a* (four-bond 'W' coupling), and tentatively assign the peak at δ 2.5 to H-1 (a normal one-dimensional homonuclear decoupling experiment in which the resonance frequency of this proton is saturated shows a loss of a coupling of approximately 0.6 Hz at H-2*n*).

If correlations with the bridge proton 7*a* are now considered, couplings are seen to the two bridgehead protons, to the high-field side of the 3*x*/3*n* resonance and to a proton at δ 1.85. These observations allow the assignment of the resonance at δ 1.85 to 7*s* and the high-field side of the 3*x*/3*n* resonance to 3*n* ('W' arrangement as for 2*n*). (This 'high-field' coupling is distinguished by comparing its position with that of a coupling which we know to be to 3*x*, as discussed below.)

Proton 7*s* is coupled to the protons giving rise to peaks at *ca* δ 1.18 and 1.08; these must therefore belong to 6*n* and 5*n*, although we cannot state in which order.

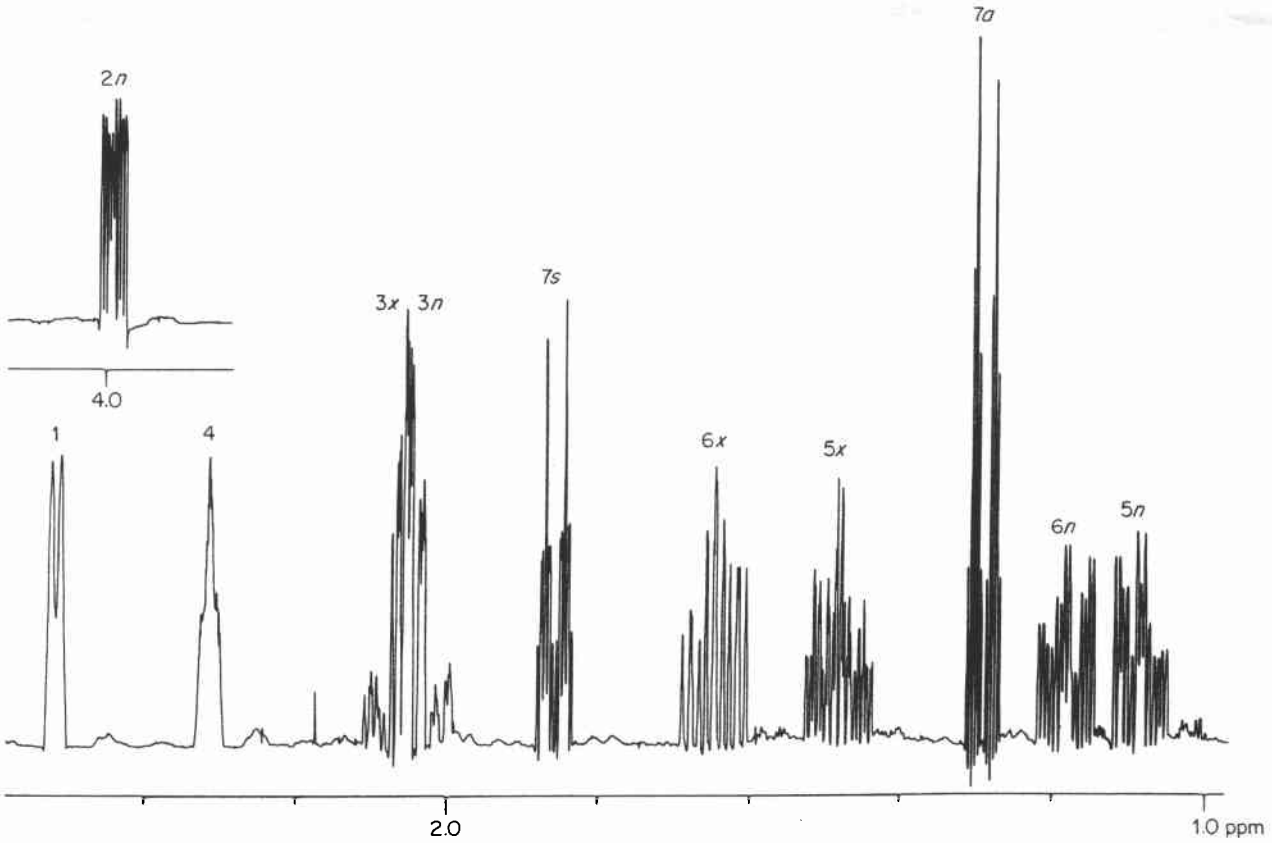

Figure 1. The 400 MHz ^{1}H NMR spectrum of 2-*exo*-bromonorbornane (0.13 M in $CDCl_3$ solution).

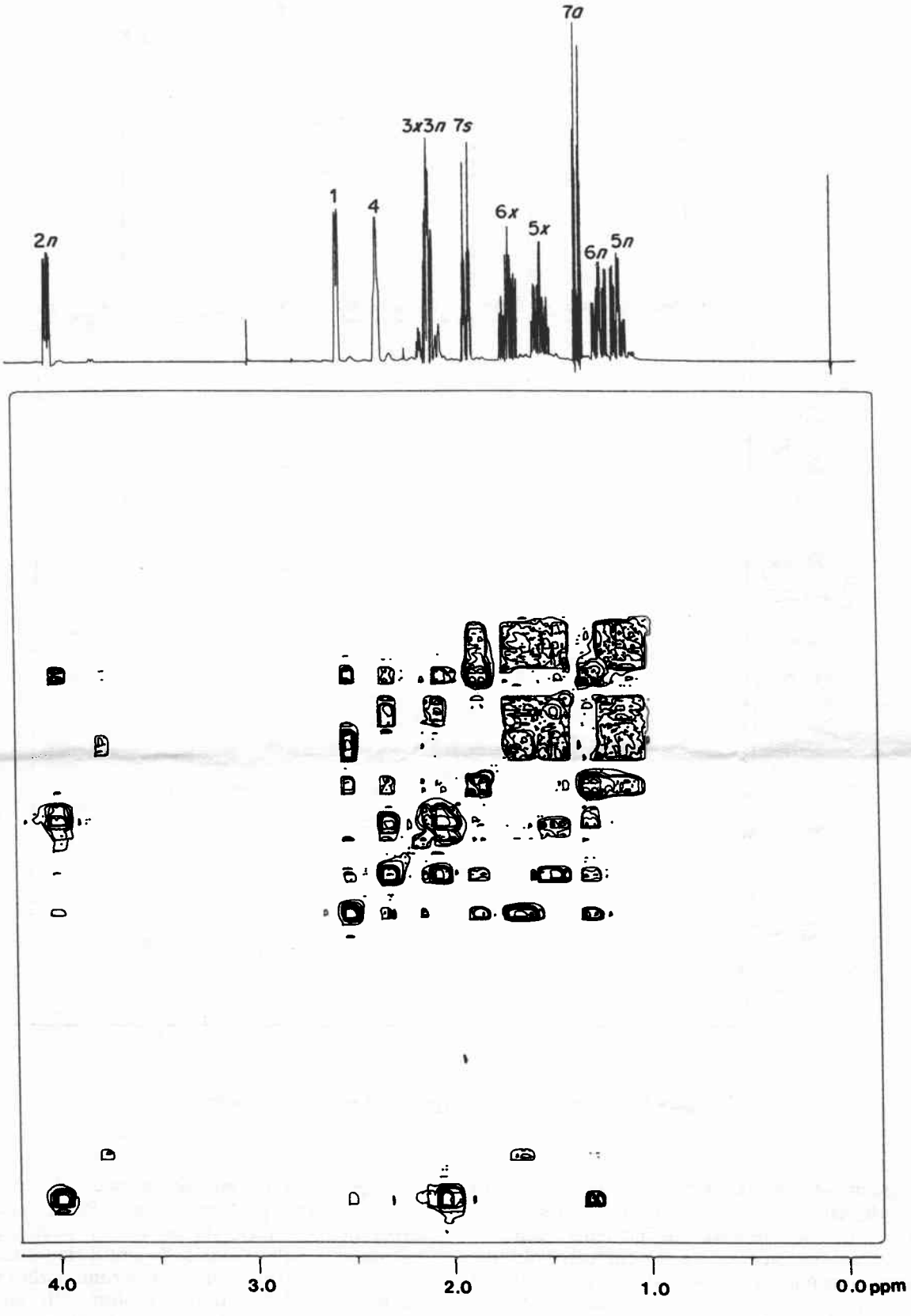

Figure 2. A COSY 2D contour plot 2-*exo*-bromonorbornane.

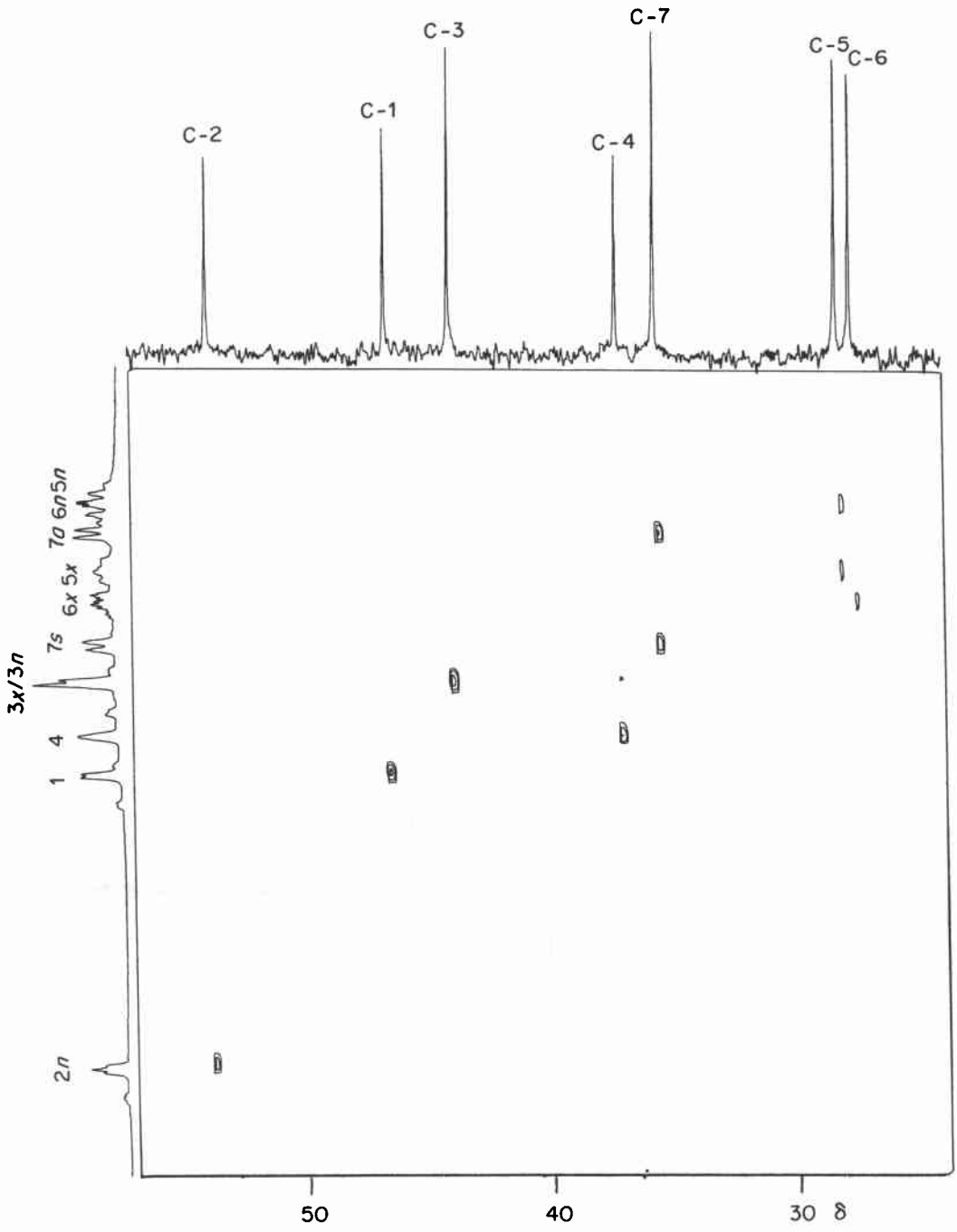

Figure 3. A $^{1}H^{13}C$ correlation diagram of 2-*exo*-bromonorbornane.

Assignment of protons $6x/5x$ is straightforward owing to the large correlation shown with the $5n/6n$ protons, and the relative assignments can be determined on the basis of their couplings with the bridgehead protons. Proton H-1 shows a strong correlation with the low-field *exo* proton (hence $6x$) and H-4 with the high-field ($5x$), the assignment of H-1 and H-4 being unambiguously determined on the basis of the observed large coupling of $3x/3n$ to the high-field (H-4) proton. Therefore, on the basis of this one two-dimensional experiment, it has been possible to assign the chemical shifts of nine of the protons and make relative assignments of the other two.

In order to distinguish between the $5n$ and $6n$ protons, we performed a $^{1}H/^{13}C$ correlation experiment[13] which shows the connectivity of the proton and carbon atoms. Figure 3 shows the results. The ^{13}C spectrum of 2-*exo*-bromonorbornane has been analysed,[14] and our proton shift assignments allow us to verify that analysis. The experiment clearly shows that the low-field *endo*-proton is attached to the same carbon atom as the 6-*exo*-proton and, hence, can be assigned as $6n$ (cf. for high-field *endo*-proton).

Although we have been able to assign all the chemical shifts, we could not directly measure accurate values for the $3x$ and $3n$ protons. To

Table 1. Proton chemical shifts (δ) for 2-*exo*-bromonorbornane (1) in various solvents

Proton	Solvent				
	C_6D_{12}	CCl_4	$CDCl_3$	$(CD_3)_2CO$	DMSO
2*n*	3.822	3.885	3.989	4.078	4.141
1	2.457	2.494	2.516	2.460	2.432
4	2.249	2.309	2.313	2.304	2.284
3*x*, 3*n*	2.028	2.041	2.070 2.030	2.048	2.000
7*s*	1.897	1.878	1.857	1.807	1.723
6*x*	1.612	1.650	1.645	1.637	1.571
5*x*	1.472	1.481	1.480	1.475	1.420
7*a*	1.237	1.273	1.289	1.308	1.276
6*n*	1.105	1.188	1.179	1.214	1.184
5*n*	1.105	1.083	1.083	1.105	1.053

overcome this problem, we treated the pattern at δ 2 as the AB part of a seven spin system to simulate the observed spectrum, using the PANIC program[15] for NMR spectral simulation. The resultant chemical shifts for the best fit are given in Table 1, together with the remaining chemical shifts for **1** obtained directly from the 400 MHz spectrum. The resolved couplings are given in Table 2. The spectrum of **1** was recorded at 250 MHz in a number of common solvents of differing polarity, and the chemical shifts directly from these spectra are also given in Table 1. In these cases the 3*x* and 3*n* system was not separately analysed, but the average chemical shift is recorded in Table 1.

The data in Table 1 are of some interest, inasmuch as the question of possible solvent effects on proton SCS has bedevilled some of the previous investigations in this field.[5] It can be seen that only two protons show any significant change in chemical shift in varying the solvent from cyclohexane to DMSO, which covers the entire range of polarity of common NMR solvents. The protons which are affected are the 2*n* and 7*s* protons. The 2*n* proton shows a significant (0.3 ppm) and continuous shift to low field with increasing solvent polarity, as would be predicted from reaction field considerations.[16] More interestingly, the 7*s* proton shows a similar continuous variation in chemical shift with solvent polarity, but in this case the effect is much smaller (0.17 ppm) and in the opposite direction, being to high-field with increasing solvent polarity. This is probably due to the unusual orientation of the 7s C—H bond, which is almost anti-parallel to the C—Br dipole and, therefore, the C—H vector is opposed to the reaction field. In this orientation, increasing the reaction field would tend to produce an upfield shift of the C—H proton, as is observed.

The remaining protons in **1** show very small changes in chemical shift with solvent (<0.1 ppm), which do not vary continuously with solvent polarity. Hence systematic solvent effects on these chemical shifts are minimal.

The proton couplings obtained for **1** generally follow the values found for multi-substituted norbornanes.[11] In particular, the vicinal couplings in the C-5—C-6 fragment agree well with those obtained by Marshall *et al.*[17] for the (deuteriated) parent hydrocarbon, indicating that the ring skeleton of **1** is unperturbed from the parent geometry.

The influence of the bromo substituent on the vicinal couplings can be seen by comparison of the C-1–C-2 and C-5–C-6 couplings. There is a pronounced decrease in the *endo–endo* coupling (9.4 → 7.0 Hz), and a much smaller decrease in the *exo–endo* coupling (4.2 → 3.5 Hz).

One previously ambiguous coupling is the H-1–H-2*n* coupling, Marchand and Rose reporting a value of 0.0 Hz in norbornene[11,18] and Marshall and Walter[19] a value of 0.12 Hz in norbornanone. Interestingly, in Ref. 18 it is shown that decoupling the bridgehead protons significantly sharpens the *endo*-protons, clearly indicating the presence of a small coupling. The 1,2-*endo* coupling is clearly observed in the COSY spectrum of **1** (Fig. 2), and the value of 0.66 Hz is obtained directly from the H-2 multiplet. This value is also consistent with the full analysis of the norbornene spectrum given in Part 1.[1] Such a small coupling could well have been obscured in the early investigations by the complex unresolved second-order splittings of this multiplet at lower applied fields.

2-Bromoadamantane (2)

The earlier analysis of the spectrum of **2** by van Deursen and co-workers[7] was based largely on

Table 2. proton–proton couplings (Hz) in 2-*exo*-bromonorbornane

Proton	Proton										
	1	2*n*	3*x*	3*n*	4	5*x*	5*n*	6*x*	6*n*	7*s*	7*a*
1											
2*n*	0.66										
3*x*	[a]	3.5									
3*n*	[a]	7.0	−14.3								
4	[a]	[a]	4.1	0.4							
5*x*	[a]	[a]	2.6	[a]	4.1						
5*n*	[a]	[a]	[a]	[a]	[a]	−11.8					
6*x*	4.2	[a]	[a]	[a]	[a]	11.9	3.8				
6*n*	0.4	[a]	[a]	[a]	[a]	4.2	9.4	−12.6			
7*s*	1.6	[a]	[a]	[a]	1.6	[a]	2.3	[a]	2.3		
7*a*	1.7	1.8	[a]	2.4	1.7	1.7	[a]	[a]	[a]	−10.0	

[a] Not resolved.

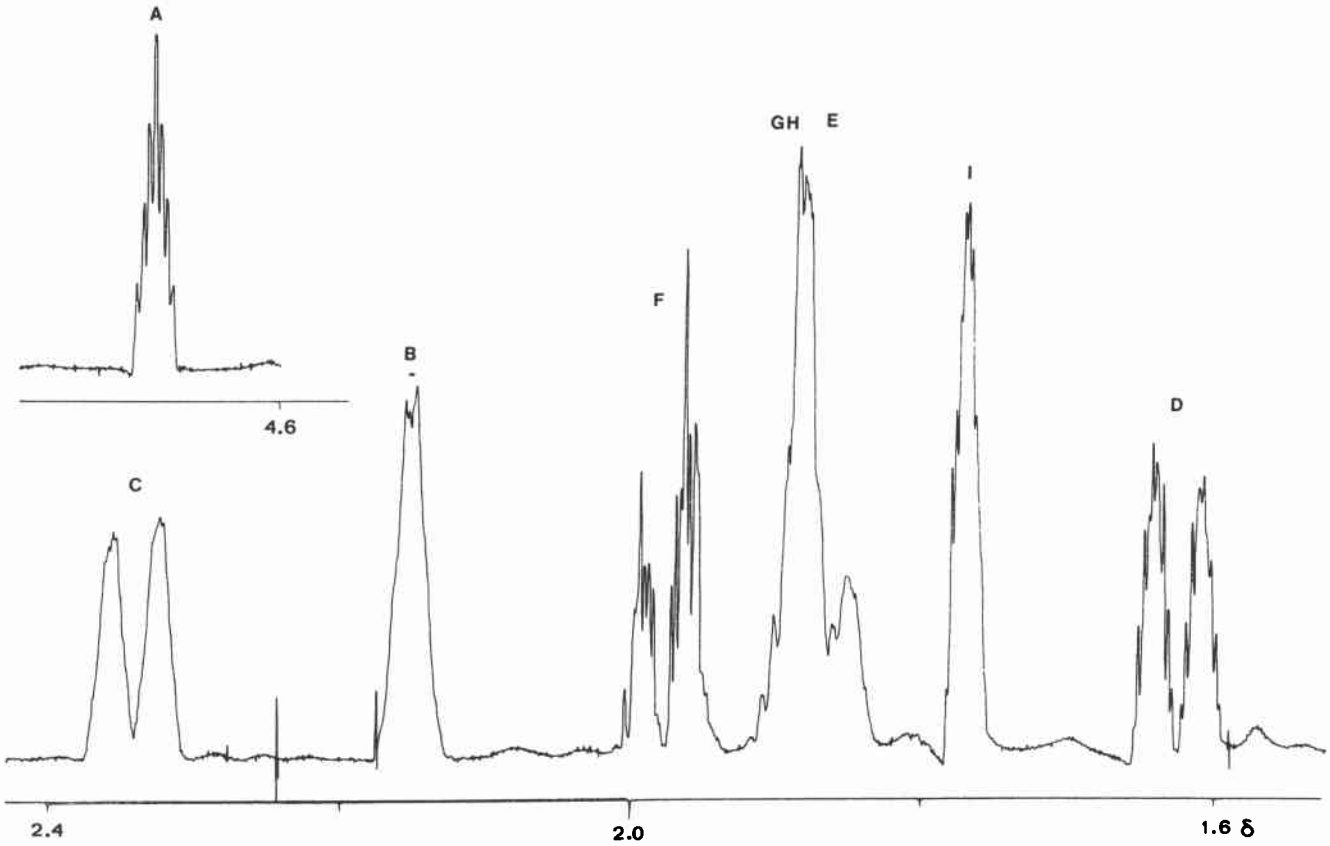

Figure 4. The 400 MHz ^{1}H NMR spectrum of 2-bromoadamantane (0.13 M in $CDCl_3$).

structural considerations. However, the spectrum can be analysed completely without making 'structural preconditions' by recording the normal (1D) spectrum (Fig. 4), a COSY 2D spectrum (Fig. 5) and one proton spin-decoupled spectrum.

The assignment of the chemical shift of proton A (geminal to the substituent) is straightforward; the other assignments follow from the COSY 2D experiment (Fig. 5). This shows couplings between proton A and the singlet at δ 2.15 and the doublet at δ 1.62. Clearly, the singlet must be assigned to B and, by virtue of the fact that of protons C, D, E and F only D bears a 'W' relationship with A which permits such long-range coupling, the doublet must be assigned to D.

Proton D shows (Fig. 5) a strong coupling to the doublet at δ 2.34 to B and to the 'three'-proton peak at δ 1.88. These observations allow us to assign proton C (geminal to D) and proton H, as of all the so far unassigned protons (E, F, G and H) only H is in a position to experience such a spin–spin coupling.

On the basis of the correlations shown to proton C we are able to assign proton I (the coupling resulting from its 'W' relationship to C is clearly visible). Therefore, the only remaining assignments to be made are those for protons E, F and G.

At *ca* δ 1.9 one part of an AB pattern is observed which can only be due to E or F. There is no observable coupling in the COSY spectrum between the proton and that of proton C, and single decoupling experiments confirmed this. As proton E but not F bears a 'W' relationship to C, we assign this low-field part of the AB pattern to proton F. The resonance of proton E is partially obscured by the broad single peak due to G and H, but the chemical shift of E can be obtained accurately from the AB analysis. The proton chemical shifts thus obtained for **2** are given, together with those of 1-bromoadamantane (**3**), in Table 3. The latter were obtained directly from the 250 MHz proton spectrum, under the same experimental conditions as the above, in order to obtain more accurate data than those presently available. The literature data for **2** and **3** are also given in Table 3. It can be seen that the unambiguous spectral assignment of **2** confirms the 'structural' assignment of Ref. 7 in all respects, which is very pleasing. There was no ambiguity over the assignment of **3** and our data are in agreement with the less accurate low-field data,[6] remembering that these shifts are accurate to *ca* $\pm$0.05 ppm. Interestingly, even at 250 MHz, the separate resonances of the δ_e and δ_a protons are not resolved, only one peak of this AB system being observed.

The bromine SCS

The data in Tables 1 and 3, when combined with the accurate proton chemical shifts for the parent hydrocarbons given in Part 1,[1] give the bromine SCS of all the protons in these molecules. The corresponding data for axial and equatorial bromocyclohexane taken from Ref. 8, and combined with the δ values for cyclohexane from Part 1[1] under the

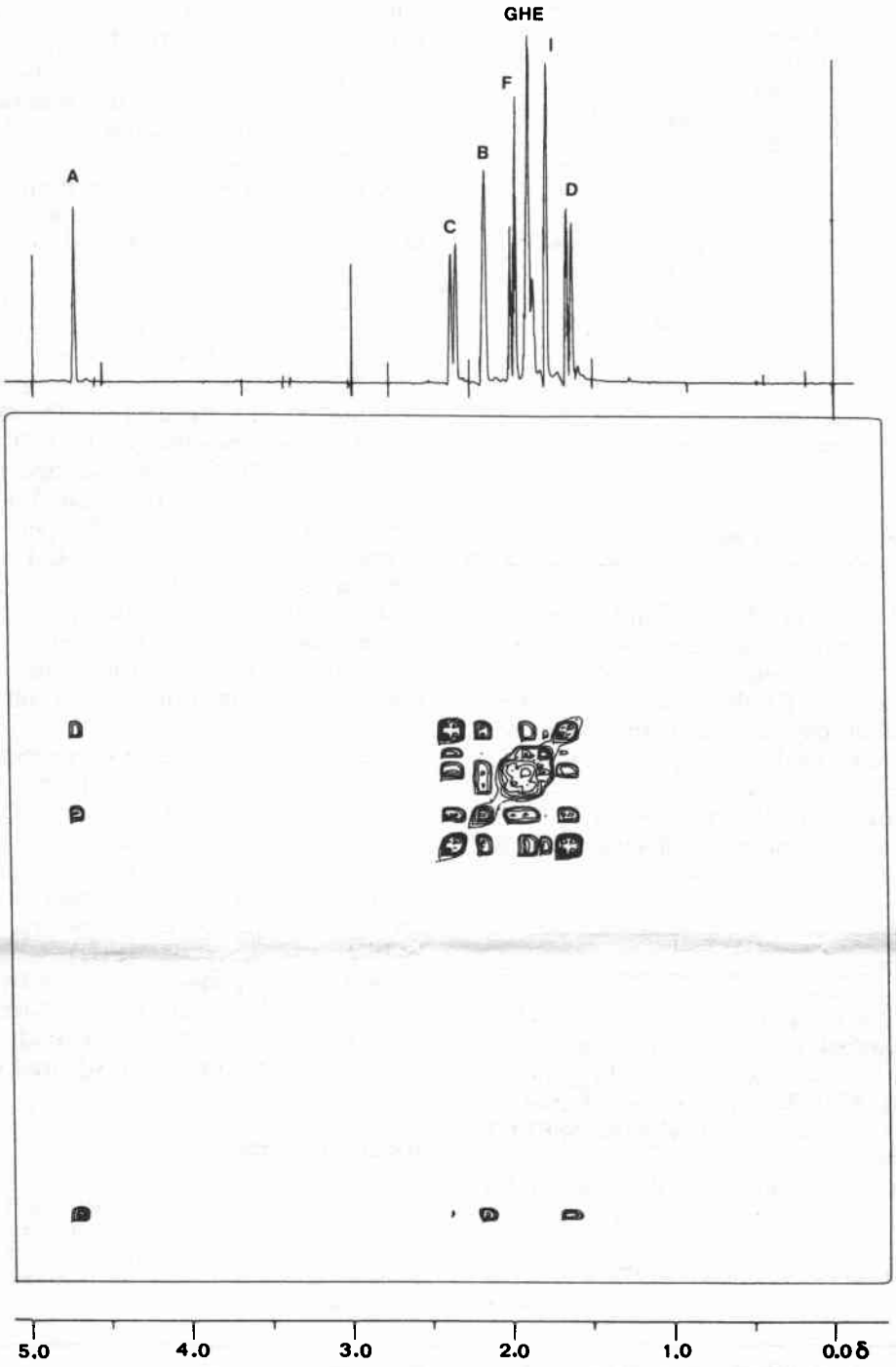

Figure 5. A COSY 2D contour plot of 2-bromoadamantane.

same conditions of solvent and temperature, are given in Table 4. For completion, the literature data[2] for methyl, ethyl, propyl, isopropyl and *tert*-butyl bromide are also included in Table 4, using the δ values of propane of 0.91 (CH_3) and 1.35 (CH_2).[20]

The collective SCS comprise a data set of 38 protons, all of which are in molecules of well defined geometry, and this data set constitutes a rigorous test of present theories of SCS.

The detailed quantitative examination of the various mechanisms proposed to account for proton SCS will be considered subsequently. It is pertinent to note here just one outstanding anomaly in all the present postulated mechanisms. The generally accepted view of bromine SCS is that they are made up of an inductive contribution plus longer range contributions due to the C—Br bond magnetic anisotropy and electric field. Van der Waals contributions from the bromine electrons are also sometimes included. No combination of these mechanisms can explain the change in SCS of the CHBr proton in bromoalkanes. In CH_3Br, EtBr and *i*-PrBr the SCS values are 2.46 (CH_3Br), 2.51 (CH_2Br) and 2.8–3.1 (CHBr). These changes in SCS are more clearly illustrated by comparison with the analogous chloro and iodo compounds. In particular,

Table 3. Proton chemical shifts (δ) for bromoadamantanes

Compound	Proton	This work[a]	Literature
2-Bromoadamantane (2)	A	4.697	4.68[b]
	B	2.150	2.13[b]
	C	2.340	2.33[b]
	D	1.623	1.62[b]
	E	1.866	1.85[c]
	F	1.973	1.97[c]
	G	1.883	1.9[b]
	H	1.883	1.9[b]
	I	1.768	1.78[d]
1-Bromoadamantane (3)	β	2.368[e]	2.30[d]
	γ	2.105[e]	2.08[d]
	δ	1.731[e]	1.73[d]

[a] Measured in $CDCl_3$ solution at 400 MHz.
[b] Ref. 7a.
[c] Ref. 7c.
[d] Ref. 6.
[e] Measured in $CDCl_3$ solution at 250 MHz.

the chemical shift (δ) of the CHX proton in isopropyl halides, 2-adamantyl halides and axial and equatorial cyclohexyl halides goes upfield on changing the substituent from I to Br to Cl, the reverse of the usual order. No quantitative explanation of this phenomenon has yet been suggested, although the idea of a steric dependence of the C—X bond magnetic anisotropy, proposed by Bothner-By and Naar-Colin,[21] is intriguing. These anomalies will be considered further in subsequent parts of this series.

EXPERIMENTAL

The ^1H NMR spectra of approximately 0.13 M $CDCl_3$ solutions (TMS internal reference) of 2-*exo*-bromonorbornane and 2-bromoadamantane (both obtained commercially from Aldrich) were recorded using a Bruker 400 WM spectrometer, fitted with the ASPECT 2000 computer system.

Both spectra (and the spin-decoupled spectra for the adamantane derivative) were obtained from FIDs recorded over 16 transients of sweep width 1200 Hz (acquisition time of 7.79 s) in 16 K memory space. The FIDs were transformed into 32 K memory space following the use of resolution enhancement factors (LB = −0.8, GB = 0.3). The digital resolution obtained was 0.128 Hz per point. The experiments were performed at 20 °C and the spin-decoupling experiments for 2-bromoadamantane involved use of decoupler powers over the range 15–10 L. Both COSY 2D experiments were performed using sweep widths of *ca* 1230 Hz in the F2 domain (615 Hz in F1), memory size in F2 of 1 K and in F1 of 512 W (zero filling in F1), over 128 experiments, each experiment involving 32 transients (with two dummy scans). The acquisition time was *ca* 0.4 s. The pulse sequence used was $90°-\tau-90°$ with $\tau \approx 4$ s. Fourier transformation in both dimensions was performed using a sine bell-squared window function. The ^1H NMR spectrum of 1-bromoadamantane (0.13 M $CDCl_3$ solution, TMS reference, at 20 °C) was recorded using the Bruker 250 WM instrument (as were the spin-decoupled spectra of 2-*exo*-bromonorbornane using decoupler powers over the range 15–18 L). The FID was acquired in 32 transients (memory size 8 K, sweep width 794.9 Hz, acquisition time 5.58 s). Resolution enhancement factors (LB = −0.4, GB = 0.3) were used prior to Fourier transformation into 32 K. Digital resolution of transformed spectrum was 0.24 Hz per point.

The ^1H–^{13}C correlation experiment was performed using a sweep width of 3970 Hz in the F2 domain (^{13}C) and 1090 Hz in the F1 domain (^1H), memory size in F2 of 1 K and in F1 of 512 W (zero filling in F1), over 256 experiments, each involving eight transients (with two dummy scans). The acquisition time was *ca* 0.13 s. The pulse sequence used was ^1H, $90°-\tau-90°$ (BB); and ^{13}C, $\tau_1-180°-\tau_2-90°$ (FID).

Proton decoupling was achieved using a decoupler power of 12 H ($\tau \approx 0.004$ s, $\tau_1 = 5.0$ s, $\tau_2 = 0.006$ s).

Fourier transformation in both dimensions was performed using a sine bell squared window function.

Acknowledgements

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Table 4. Substituent chemical shifts (SCS, ppm) for bromo compounds[a]

2-*exo*-Bromonorbornane (1)		2-Bromoadamantane (2)		1-Bromoadamantane (3)		1-ax-Bromocyclohexane (4)		1-eq-Bromocyclohexane (4)	
Proton	SCS	Proton	SCS	Proton	SCS	Proton	SCS	Proton	SCS
1	0.324	A	2.924	β	0.615	1eq	3.097	1ax	2.839
2	2.827	B	0.276	γ	0.231	6eq	0.353	6eq	0.606
3*x*	0.599	C	0.587	δ	−0.022	6ax	0.576	6ax	0.523
3*n*	0.868	D	−0.130						
4	0.122	F	0.220	Proton	Methyl[b]	Ethyl[b]	*n*-Propyl[b]	*i*-Propyl[b]	*t*-Butyl[b]
5*x*	0.009	E	0.113	α	2.46	2.51	2.44	2.86	
5*n*	−0.079	G	0.009	β		0.60	0.54	0.82	0.67
6*x*	0.174	H	0.009	γ			0.15		
6*n*	0.017								
7*s*	0.675								
7*a*	0.107								

[a] For δ values of parent compounds, see Ref. 1.
[b] See Ref. 2.

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