

^{29}Si AND ^{13}C NMR SPECTRA OF TRIMETHYLSILOXY AND HYDROXY ADAMANTANES REINVESTIGATED AT LOW CONCENTRATION IN DEUTERIOCHLOROFORM SOLUTIONS

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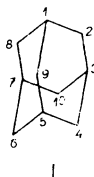
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^{29}Si and ^{13}C NMR chemical shifts are reported for mono- and bis(trimethylsiloxy)adamantanes as well as for mono- and dihydroxyadamantanes dissolved in deuteriochloroform. The chloroform induced changes in ^{29}Si and ^{13}C chemical shifts can be qualitatively accounted for by hydrogen-bonding considering basicity and solvent accessibility of oxygen atoms in the solute molecules. The steric effects observed on the ^{29}Si shifts are not due to an interaction of the terminal hydrogen atoms of the trimethylsilyl groups but are due to proximity of two oxygen atoms on one cyclohexane ring of the adamantane skeleton.

Several years ago we investigated NMR spectra of series of trimethylsiloxy substituted steroids¹ and adamantanes² by the experimental technique available at that time. The results have shown that the ^{29}Si NMR chemical shifts are influenced to a large extent by steric factors in both classes of compounds. However, detailed interpretation of the silicon chemical shifts in structural terms was satisfactory only for adamantane derivatives (measured in concentrated tetrachloromethane solutions). Similar attempts to rationalize the shifts in steroids (measured as neat compounds) have been unsuccessful until recently when it has become technically feasible to measure the solution spectra at a much lower concentration.

The ^{29}Si chemical shifts of 3 ξ -trimethylsiloxy-5 ξ -cholestanes measured in dilute deuteriochloroform solutions fall into two distinct ranges with clear stereochemical interpretation³. It is, therefore, of interest to see whether the accepted interpretation^{2,4} holds for the adamantane *I* derivatives if they are measured under the conditions that yield interpretable results for the steroids³.



RESULTS AND DISCUSSION

²⁹Si Chemical Shifts

Juxtaposition of silicon chemical shifts in deuteriochloroform solutions (Table I) with the shifts in tetrachloromethane solutions² show that in all cases chloroform induces paramagnetic shifts (i.e. larger shift values or downfield shifts). Such paramagnetic shifts are in agreement with the notion of hydrogen bonding between chloroform and oxygen atoms in siloxyadamantanes, though some part of the observed shift difference might be due to different method of referencing.

The chloroform induced shifts are smaller (0.4–0.8 ppm) for the silicon atoms, Si(*s*), attached to secondary adamantane carbon atoms and larger (1.2–1.6 ppm, excluding 1,2-derivative) for the silicon atoms, Si(*t*), attached to tertiary adamantane carbon atoms. This trend is in agreement both with the basicity and with the relative accessibility of the oxygen atoms to the solvent in the discussed compounds. The basicity of 1- and 2-trimethylsiloxyadamantane, measured as the association shift of phenol OH stretching frequency, $\Delta\nu$, is 249 and 246 cm⁻¹, respectively⁵. The

TABLE I
²⁹Si and ¹³C NMR chemical shifts of trimethylsilyl groups in trimethylsiloxy-substituted adamantanes^a

Subst. ^b	$\delta(^{29}\text{Si})$		$\delta(^{13}\text{C})$	
	Si(<i>t</i>) ^c	Si(<i>s</i>) ^c	C(<i>t</i>) ^c	C(<i>s</i>) ^c
1	7.69(0.00)	—	2.98	—
2	—	13.26(0.00)	—	0.26
1,2	7.72(0.03)	14.05(0.79)	3.01	0.58
1,3	8.30(0.61)	—	2.88	—
1,4 ^A	7.97(0.28)	13.72(0.46)	2.92	0.25
1,4 ^E	8.03(0.34)	13.97(0.71)	2.92	0.20
2 ^A ,4 ^A	—	11.91(−1.35)	—	0.32
2 ^A ,4 ^E	—	13.81(0.55) ^d	—	0.17 ^d
	—	13.85(0.59) ^d	—	0.26 ^d
2,6	—	13.49(0.23)	—	0.27

^a The chemical shifts are in δ -scale (in ppm relative to TMS). The values in parentheses are SCS values, i.e. the shifts relative to the monosubstituted adamantanes. ^b Position(s) of trimethylsiloxy group(s) on the adamantane skeleton *I*. ^c The indices *s* and *t* denote trimethylsiloxy groups on secondary and tertiary adamantane carbon atoms, respectively. ^d The assignment is uncertain.

oxygen atom O(*t*) which is bonded to adamantane tertiary carbon is equatorial in all three cyclohexane rings that share the tertiary carbon atom. In contrast, the oxygen atom O(*s*) which is bonded to a secondary adamantane carbon atom is always axial in one of the two rings that share the secondary carbon atom. Proximity of other axial substituents (hydrogen atoms) in this ring reduces accessibility of the O(*s*) oxygen atom for the solvent and, hence, the induced shifts are smaller.

Anomalous small solvent induced shift observed on Si(*t*) in the 1,2-derivative is apparently due to the adjacent bulky trimethylsiloxy group on C-2 carbon which reduces solvent accessibility of the O(*t*) oxygen atom bonded to C-1 carbon atom. The already low accessibility of the O(*s*) oxygen atom on the C-2 carbon atom can be reduced only little (if at all) by the bulky group on the C-1 carbon and so the solvent induced shift on Si(*s*) in this compound fits the general trend.

Following the arguments of ref.², the effects of the "second" substituent in bis(trimethylsiloxy)adamantanes can be discussed using the ²⁹Si SCS (substituent chemical shifts) values given also in Table I (in parentheses). Accordingly, the effect of the second substituent is either essentially the same or smaller by about 20% in deuteriochloroform than in tetrachloromethane solution. Again, the 1,2-derivative is exceptional as its SCS for Si(*t*) is reduced considerably more.

These observations are in harmony with the chloroform induced chemical shifts discussed above. If a bis(trimethylsiloxy)adamantane is hydrogen bonded to the same extent as the (mono) trimethylsiloxyadamantane used for the determination of the ²⁹Si SCS value, the SCS value is roughly the same in chloroform as in the aprotic tetrachloromethane. If, however, the bis(trimethylsiloxy)adamantane is hydrogen bonded to a lesser extent than the mono derivative, the SCS value is reduced. Thus the large reduction of the SCS value for Si(*t*) in 1,2-derivative is explained by the steric hindrance due to the second trimethylsiloxy group discussed above. If we accept this interpretation, we are led to a seemingly surprising conclusion about hydrogen bonding in 2^A,4^A-bis(trimethylsiloxy)adamantane. Since in this compound the (negative) SCS value is the same in the two solvents, we must conclude that the two axial oxygen atoms in 2,4 arrangement are hydrogen bonded to the same extent as the oxygen atom in 2-trimethylsiloxyadamantane. Though this at first appears rather unlikely one should recall that the oxygen atom in 2-trimethylsiloxyadamantane is already sterically hindered as discussed above.

The solvent effect that we have just discussed do not change the main findings of the previous work. The ²⁹Si chemical shift ranges of Si(*s*) and Si(*t*) silicon atoms are well separated and Si(*t*) remains more shielded. The latter observation was attributed to steric interaction with hydrogen atoms on γ positioned CH groups. The diamagnetic shift of the silicon in 2^A,4^A-bis(trimethylsiloxy)adamantane that is caused by steric interaction has remained anomalous and the inductive effect compensates similar steric diamagnetic shifts in 1,2-bis(trimethylsiloxy)adamantane in deuteriochloroform as in tetrachloromethane solutions.

TABLE II
¹³C NMR chemical shifts δ and deviations Δ from additivity in trimethylsiloxy-substituted adamantanes^a

Subst. ^b	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
—	28.36	37.77								
1	71.40	46.04	30.92	36.24	30.92	36.24	30.92	46.04	46.04	36.24
2	35.27	74.95	35.27	31.22	37.67	37.79	27.22	36.65	31.22	36.65
1,2	73.56	78.78	37.72	30.00	30.15	36.55	30.51	45.16	39.02	35.76
	Δ (-4.75)	-4.44	-0.11	0.31	-0.08	0.29	0.73	0.24	-0.47	0.64
	$\langle \Delta \rangle$ (-0.92)	-1.26	0.01	-0.26	1.03	0.11	0.03	0.02	-1.39	-0.77
1,3	73.38	54.24	73.38	44.75	31.38	34.84	31.38	44.75	44.75	44.75
	Δ (-0.58)	-0.07	-0.58	0.24	-2.10	0.13	-2.10	0.24	0.24	0.24
	$\langle \Delta \rangle$ (-0.48)	0.55	-0.48	-0.40	-0.60	0.43	-0.60	-0.40	-0.40	-0.40
1,4 ^A	70.96	39.52	38.08	73.08	38.08	35.09	29.72	46.10	39.52	35.09
	Δ (0.70)	0.03	0.25	-0.34	0.25	-0.03	-0.51	0.04	0.03	-0.03
	$\langle \Delta \rangle$ (-0.02)	0.69	-0.41	-0.42	-0.41	-0.47	-0.29	-0.12	0.69	-0.47
1,4 ^E	70.79	44.37	37.14	73.83	37.14	29.88	30.17	46.21	44.37	29.88
	Δ (0.19)	-0.55	-0.69	0.41	-0.69	0.19	-0.06	0.15	-0.55	0.19
	$\langle \Delta \rangle$ (-0.29)	-0.11	-0.06	0.01	-0.06	-0.15	-0.03	0.06	-0.06	-0.15
2 ^A ,4 ^A	35.46	75.57	41.08	75.57	35.46	37.00	26.42	37.00	25.12	35.90
	Δ (0.88)	7.17	-1.10	7.17	0.88	0.33	0.34	0.33	0.45	0.37
	$\langle \Delta \rangle$ (-0.49)	1.85	0.19	1.85	-0.49	0.03	0.18	0.03	1.07	0.08
2 ^A ,4 ^E	34.47	76.29	42.48	69.96	34.75	31.23	26.52	36.46	30.38	30.54
	Δ (0.34)	2.46	0.30	1.56	0.17	-0.01	-0.01	-0.20	0.28	0.44
	$\langle \Delta \rangle$ (-0.24)	-0.41	-0.31	-0.41	-0.46	-0.46	0.29	0.37	0.78	0.20
2,6	34.67	74.80	34.11	30.22	34.67	74.80	34.11	30.22	24.74	35.15
	Δ (0.09)	-0.17	-0.02	0.12	0.09	-0.17	-0.02	0.12	0.07	-0.38
	$\langle \Delta \rangle$ (-0.26)	0.25	0.20	0.34	-0.26	0.25	0.20	0.34	-0.30	0.39

^a The chemical shifts are in δ -scale (ppm units relative to TMS). The lines in parentheses are the deviations Δ and $\langle \Delta \rangle$ from the values calculated according to the direct additivity using the SCS values and the shifts in trimethylsiloxyadamantanes or dihydroadamantanes, respectively, see Table IV footnotes ^c and ^e; a positive deviation indicates that the experimental shift is larger than that calculated. ^b Position(s) of the trimethylsiloxy group(s) on the adamantane skeleton, for the numbering of the carbon atoms see I.

TABLE III
¹³C NMR chemical shifts δ and deviations Δ from additivity in hydroxy adamantanes^a

Subst. ^b	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
—	28.36	37.77								
1	67.85	44.80	30.50	35.90	30.52	35.90	30.50	44.80	44.80	35.90
2	34.14	74.00	34.14	30.67	27.37	37.36	26.94	36.26	30.67	36.26
1,2	69.8 (-3.8)	77.85 -3.18	36.16 -0.12	29.53 0.73	30.46 0.95	35.67 0.18	29.84 0.85	43.51 0.22	38.62 0.92	35.80 1.41)
1,3	69.89 Δ (-0.10)	52.31 0.48	69.89 -0.10	43.57 0.64	31.14 -1.50	34.59 0.56	31.14 -1.50	43.57 0.64	43.57 0.64	43.57 0.64)
1,4 ^A	67.13 Δ (0.27)	38.42 0.72	36.94 0.66	72.21 0.08	36.94 0.66	34.83 0.44	29.31 0.23	44.55 0.16	38.42 0.72	34.83 0.44)
1,4 ^E	66.67 Δ (0.24)	42.63 -0.66	35.53 -0.75	72.53 0.40	35.53 -0.75	29.14 0.34	29.48 -0.03	44.48 0.09	42.63 -0.66	29.14 0.34)
2 ^A ,4 ^A	34.52 Δ (1.37)	75.92 9.02	38.63 -1.29	75.92 9.02	34.52 1.37	36.15 0.30	25.68 0.16	36.15 0.30	25.09 1.52	35.04 0.29)
2 ^A ,4 ^E	33.30 Δ (0.58)	75.36 2.87	40.53 0.61	68.87 1.97	33.78 0.63	30.71 0.45	26.23 0.28	36.01 0.16	30.22 1.06	29.80 0.64)
2,6	33.50 Δ (0.35)	73.67 0.08	32.90 0.18	29.62 0.46	33.50 0.35	73.67 0.08	32.90 0.18	29.62 0.46	24.19 0.62	34.76 0.01)

^a The chemical shifts are in δ -scale (ppm units relative to TMS). The lines in parentheses are the deviations Δ from the values calculated according to the direct additivity; a positive deviation indicates that the experimental shift is larger than that calculated. ^b Position(s) of the hydroxy group(s) on the adamantane skeleton, for the numbering of the carbon atoms see I.

¹³C Chemical Shifts

Methyl carbon chemical shifts are not substantially affected by the solvent; the regions of chemical shifts of C(*t*) and C(*s*) remain well separated in deuteriochloroform solutions. Data in Table I show the shifts to be 0.03–0.07 ppm larger in deuteriochloroform solutions than those reported earlier^{2,4} (exceptions being 2-trimethylsiloxyadamantane and 2^A,4^E-bis(trimethylsiloxy)adamantane in which the differences are +0.23 and –0.05 ppm, respectively). The small observed solvent effects are in harmony with the distance of the methyl group from the possible site of solvation and with the so-called insulating effect of silicon atom noted on some other occasions⁶. In connection with possible interpretation of steric effects one notices that in the compounds with the most acute crowding (i.e. in 1,2- and 2^A,4^A-bis(trimethylsiloxy)adamantanes) the methyl carbons are shielded least. However, the differences in the shieldings are too small to warrant meaningful discussion. They are also too small to explain the steric effect observed on ²⁹Si chemical shifts by the interaction of the terminal hydrogen atoms of the trimethylsilyl groups in a way analogous to the Grant–Cheney⁷ mechanism.

Adamantane skeleton carbon chemical shifts are assembled in Tables II and III. Following the pattern of previous studies^{2,4} included are also the deviations Δ of the experimental values from the shifts calculated according to the direct additivity rule⁸ using SCS values given in Table IV. Comparison with the earlier results^{2,4}

TABLE IV
¹³C Substituent chemical shifts in substituted adamantanes^a

Subst. ^b	α	β	γ_{syn}	γ_{anti}	δ_{syn}	δ_{anti}	ϵ
(CH ₃) ₃ SiO (<i>t</i>) ^c	43.04	8.27	—	2.56	—	–1.53	—
(<i>s</i>) ^c	37.18	6.91	–6.55	–1.12	–0.69	–1.14	0.02
HO (<i>t</i>) ^d	39.49	7.03	—	2.14	—	–1.87	—
(<i>s</i>) ^d	36.23	5.78	–7.10	–1.51	–0.99	–1.42	–0.41
(CH ₃) ₃ Si (<i>t</i>) ^e	3.55	1.24	—	0.42	—	0.34	—
(<i>s</i>) ^e	0.95	1.13	0.55	0.39	0.30	0.28	0.43

^a Substituent chemical shifts (SCS) calculated as the difference between the observed shifts of the corresponding carbons in the monosubstituted and the parent adamantane derivative. ^b Indices (*t*) and (*s*) indicate position of the substituent on tertiary and secondary adamantane carbon atoms, respectively. ^c SCS values used in connection with the chemical shifts in adamantane to calculate the shifts in bis(trimethylsiloxy)adamantanes. ^d SCS values used in connection with the chemical shifts in adamantane to calculate the shifts in dihydroxyadamantanes. ^e SCS values used in connection with the chemical shifts in dihydroxyadamantanes to calculate the shifts in the corresponding bis(trimethylsiloxy)adamantanes.

shows that the solvent does not appreciably affect the agreement with the experiment. The deviations remain large for the substituted carbon atoms in the 1,2-, 2^A,4^A-, and 2^A,4^E-derivatives. However, the present data allow a different application of the direct additivity rule. The carbon shifts in bis(trimethylsiloxy) derivatives can be also calculated from the shifts in the corresponding dihydroxyadamantane using the SCS values of trimethylsilyl group. Using this modified procedure the large deviations found for substituted carbons in 1,2- and 2,4-bis(trimethylsiloxy)-adamantanes are substantially reduced (by some 70%, see $\langle \Delta \rangle$ values on Table II). This finding supports our earlier suggestion that it is an oxygen–oxygen non-bonding interaction that is responsible both for the large deviations in hydroxy and trimethylsiloxy adamantane derivatives and for the observed effects of crowding on the ²⁹Si chemical shifts in the latter compounds.

On the other hand for some other carbon atoms the modified method of calculation yields values that agree with the experiment worse (compare the Δ and $\langle \Delta \rangle$ values, Table II). Apparently, the procedure is not very suitable for calculation of the shifts in disubstituted derivatives when solvation can influence the shifts in the model and in the disubstituted compounds differently.

Conclusion

The chloroform induced changes in ²⁹Si and ¹³C chemical shifts are small; their direction and relative magnitude are predictable if hydrogen bonding between the solvent and oxygen atoms of the solute is considered to be affected by basicity and solvent accessibility of the oxygen atoms.

The present result lends further support to earlier interpretation of steric ²⁹Si chemical shifts. The steric shifts are not caused by an interaction of the terminal hydrogen atoms of the two trimethylsilyl groups but are due to the proximity of two oxygen atoms that are bonded to one cyclohexane ring of the adamantane skeleton.

From the point of view of analytical applications, the use of protic solvent appears not to be advantageous as the effect of hydrogen bonding can partially compensate the steric effects.

EXPERIMENTAL

Synthesis and isolation of the studied adamantane derivatives were described previously^{2,4}. The samples were measured as 0.04–0.3M solutions in deuteriochloroform which contained 2% (v/v) of hexamethyldisilane (HMDSS). HMDSS served two purposes: first, it provided a reference for ²⁹Si NMR spectra ($\delta = -19.79$) and, second, it served to check on sufficient dilution of the samples as explained below.

All reported NMR data were obtained on a Varian XL-200 spectrometer operating at 39.7 and 50.6 MHz for ²⁹Si and ¹³C NMR, respectively. The chemical shifts are accurate within ± 0.02 ppm. ¹³C NMR spectra were measured using standard one-pulse sequence with spectral width 16 kHz, acquisition time 1.0 s and relaxation delay 1.0 s. Before Fourier transformation

the FID data were exponentially weighed with line broadening of 3.0 Hz, 32 Kb of data points were used in the transform. The spectra were referenced to the line of the solvent ($\delta = 76.99$). In order to verify the line assignments published previously^{2,4}, ¹³C APT spectra⁹ were also measured.

²⁹Si NMR spectra were recorded using an earlier described modification of INEPT pulse sequence¹⁰. Acquisition time of 1.0 s, relaxation delay of 5.0 s, spectral width of 4.0 kHz, line broadening of 1.0 Hz, and 16 Kb of memory were employed. The lines in 1,2-, 1,4^A, and 1,4^E-bis(trimethylsiloxy)adamantanes were assigned on the basis of SPINEPTR experiments¹¹ with improved phase cycling¹².

When deuteriochloroform line is used as ¹³C reference, care should be taken that the solvent is present in a sufficient excess. Otherwise, hydrogen bonding between the solvent and solute shifts the reference line and then the reported chemical shifts show concentration dependence. Such concentration effects are manifested also on the ¹³C NMR line of HMDSS which is shifted by the hydrogen bond between the solvent and solute to more negative δ values. Hence, in the present study the ¹³C chemical shift of HMDSS served as a monitor of dilution. The solutions were repeatedly diluted until the ¹³C NMR chemical shift of HMDSS reached the value $\delta = -2.47 \mp 0.02$ which is the chemical shift of HMDSS in binary mixtures of CDCl₃ and HMDSS.

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