

NMR SPECTRA OF SOME SECONDARY SUBSTITUTED ADAMANTANES

PART I. 2-MONO-SUBSTITUTED ADAMANTANES

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The NMR spectra of tertiary substituted adamantanes have been extensively discussed by F.C. Fort and P. von R. Schleyer (1).

In the present article we want to discuss the NMR spectra and substituent shifts of some 2-mono-substituted adamantanes, which have lower symmetry than 1-mono-substituted adamantanes.

There are nine different kinds of protons in 2-mono-substituted adamantanes (Fig. 1).

Between these protons the following coupling constants are to be expected :

1. $J(\text{gem}) = 11 - 13 \text{ Hz}$, as in cyclohexanes (2).
2. $J(\text{vic}) = 2.6 \text{ Hz}$, in all cases equal, as in tertiary substituted adamantanes (1).
3. $J(\text{long range}) = 1 \text{ Hz}$, coupling over four bonds in a W-arrangement (3).

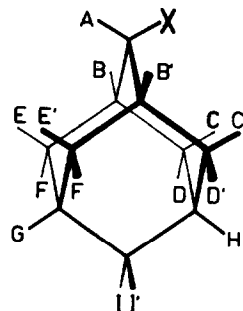


FIGURE 1

All possible spin interactions are given in Table I.

TABLE I
Possible Spin-Spin Interactions ^{a)}

proton	geminal	vicinal	long range
A		BB'	DD'
BB'		ACDEF (AC'D'E'F')	GH (GH)
CC'	D (D')	BH (B'H)	EI' (E'I)
DD'	C (C')	BH (B'H)	A (A)
EE'	F (F')	BG (B'G)	CI' (C'I)
FF'	E (E')	BG (B'G)	
G		EE'FF'II'	BB'H
H		CC'DD'II'	BB'G
II'		GH (GH)	E'C' (EC)

^{a)} Protons in brackets couple with protons of the first column marked with a prime.

For this investigation we selected 2-hydroxy-, 2-amino-, 2-chloro-, 2-bromo- and 2-iodoadamantane. The spectra measured at 100 MHz are given in Fig. 2, a - e. Due to long-range and virtual (4) coupling, all absorptions appear as broad bands in which vicinal coupling constants are not detectable. All signals appear in the same region ($\delta 1.5 - \delta 2.5$), with the exception of the signal produced by proton A, which facilitates its identification.

In all spectra an "AB" system with $J = 12$ Hz is observed. This "AB" system is confirmed by comparison with the spectra at 60 MHz and by spin-tickling. Based on chemical-shift differences, this "AB" system must belong to the protons C and D rather than to the protons E and F. Then the down-field part must arise from the protons C, because protons in a 1,3-diaxial position with respect to the substituent are more strongly deshielded (5).

Only in the case of 2-hydroxyadamantane is the other "AB" system observable, with $J = 12$ Hz arising from the protons E and F.

FIG. 2a 2-Chloroadamantane a)

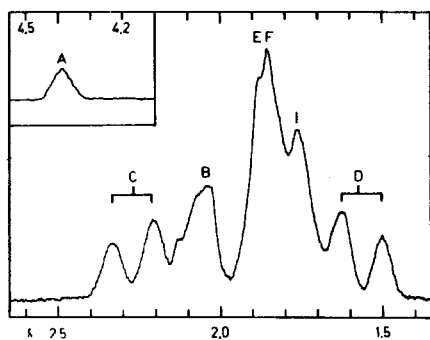


FIG. 2d 2-Hydroxyadamantane ab)

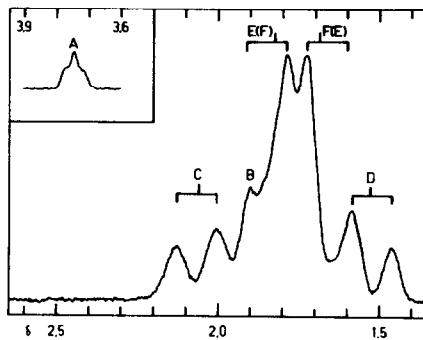


FIG. 2b 2-Bromoadamantane a)

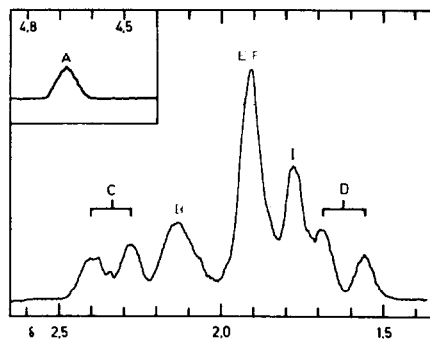


FIG. 2e 2-Aminoadamantane ab)

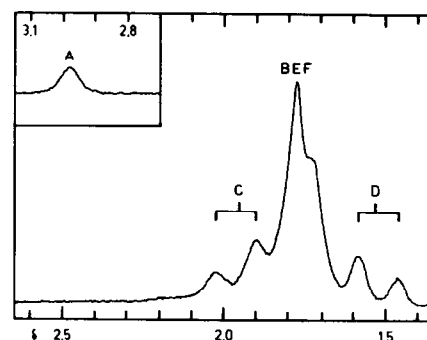


FIG. 2c 2-Iodoadamantane a)

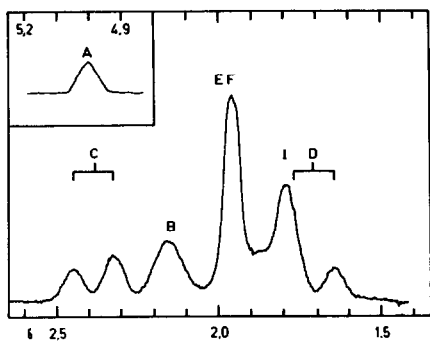
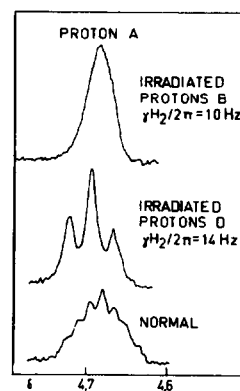


FIG. 3 2-Bromoadamantane a)



a) Measured as 5% solutions in deuteriochloroform on a Varian HA 100 with TMS as internal standard.

b) OH and NH₂ protons removed by deuteration.

In the other cases where only one strong band is observed, the frequency difference between protons E and F must be less than about 8 Hz. Therefore the chemical shift of this band furnishes only the mean chemical shift of E and F.

The signal from the protons B was identified by double resonance. By irradiating proton A the signals of the protons B and D sharpened slightly. By irradiating proton B the signal of A became a sharper singlet (Fig. 3). By irradiating proton D the signal of A became a sharp triplet, with $J = 2.6$ Hz.

In the spectra of the halogen derivatives a relatively sharp band of more than two protons is present on the up-field side of the absorption band of the protons E and F. This band belongs to the protons I, as the band of two residual protons G and H should be much broader because of their many vicinal spin interactions. It is found by accurate integration that the absorptions of G and H are hidden under and between the signals from the protons E, F, and I. In the case of 2-hydroxy- and 2-aminoadamantane the absorptions of the protons I, G, and H are hidden under the signals of E and F.

Chemical shifts and the corresponding substituent shifts are given in Table II.

TABLE II

Chemical Shifts and Substituent Shifts in 2-Substituted Adamantanes

subst.	chemical shift (ppm from TMS)								substituent shift ^{a)}				
	A	B	C	D	E (F)	GH	I	B	C	D	E (F)	I	
NH ₂	2.98	1.8	1.95	1.53	1.77	1.8	1.7		0.20	-0.22	0.02		
OH	3.75	1.89	2.06	1.53	1.82	1.69	1.8	1.7	0.04	0.31	-0.22	0.07	-0.06
Cl	4.39	2.05	2.27	1.57	1.86	1.8	1.76		0.20	0.52	-0.18	0.11	0.01
Br	4.68	2.13	2.33	1.62	1.91	1.9	1.78		0.28	0.58	-0.13	0.16	0.02
I	5.00	2.16	2.38	1.71	1.95	1.9	1.79		0.31	0.63	-0.04	0.20	0.04

^{a)} A negative sign means an up-field shift. For the chemical shifts for secondary and tertiary protons in adamantane $\delta 1.75$ and $\delta 1.85$ are used.

Relatively little is known about substituent shifts of ring-bound protons in cyclohexane chairs, in contrast to substituent shifts of protons of methyl groups substituted in cyclohexane chairs (e.g. methyl groups in steroids (6)). The trend and values of the substituent shift of the protons D are remarkable (Table II).

The 1,3-diaxial deshielding due to OH and Cl in adamantanes appears to be smaller than the deshielding by the same substituents in steroids (Table III). The vicinal substituent shift has the same trend but gives somewhat lower values as compared with 1-substituted adamantanes (Table III). A curious fact is the opposite substituent shift due to the OH-group found in steroids. The trend of the 1,3-di-equatorial substituent shift is opposite for 1- and 2-substituted adamantanes (Table III). A possible explanation of this unexpected behaviour of 1-substituted adamantanes has been given by Fort and von R. Schleyer (1).

TABLE III
Comparison of Substituent Shifts ^{a)}

subst.	1,3-diaxial		1,3-di-equatorial		vicinal		
	Ad 2 ^{b)}	steroids ⁽⁴⁾	Ad 2 ^{b)}	Ad 1 ^{c)} (1)	Ad 2 ^{b)}	Ad 1 ^{c)} (1)	steroids ^{d)} (4)
OH	0.31	0.45	0.07 (-0.06)	0.24	0.04	0.09	-0.29
Cl	0.52	0.63	0.11	0.23	0.20	0.33	
Br			0.16	0.20	0.28	0.52	
I			0.20	0.09	0.31	0.58	

a) A negative sign means an up-field shift.

b) Ad 2 = 2-substituted adamantanes.

c) Ad 1 = 1-substituted adamantanes.

d) Shift of an equatorial proton due to an axial substituent.

In a following paper we shall discuss the substituent shifts in more detail and in relation to the stereochemical configuration of 2,4-disubstituted adamantanes.

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