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LOW FIELD CHEMICAL SHIFTS IN ^{13}CARBON NMR SPECTRA OF 1,3-DEHYDROADAMANTANE COMPOUNDS POSSESSING "INVERTED CARBON ATOMS"

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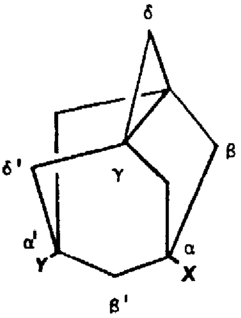
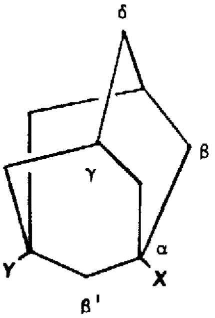
Abstract. 1,3-Dehydroadamantanes, which possess "inverted carbon atoms" in a cyclopropyl moiety, display low field ^{13}C-NMR chemical shifts for carbon atoms situated across from the cyclopropyl group. This long range effect also shows in 2,4-dehydroadamantane and is therefore not due to the presence of especially strained inverted carbons.

Some unusual ^{13}C-NMR chemical shifts for a compound possessing "inverted carbon atoms"[1] have recently been pointed out.[2] Relative to the unstrained parent compound, the introduction of an especially strained cyclopropane ring into a homoadamantane ring system resulted in chemical shifts to lower field for some remote carbon atoms. The effect was attributed to a special electronic influence of the three-membered ring containing the inverted carbons operating through intervening σ bonds.[2]

We wish to report the ^{13}C-NMR spectra of some 1,3-dehydroadamantanes[3] (**1**) which possess inverted carbons and point out that they also show unusually low field chemical shifts.



1



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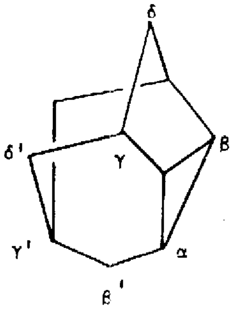

3

The spectral assignments, given in the Table, of chemical shifts of the 1,3-dehydroadamantanes **1** (for X=Y=H, X=Y=CH_3 and X=H, Y=CN) were made firstly on the basis of C-H splittings in the hydrogen coupled spectra and then by intensities of adsorption. For example, the lowest field adsorption of the unsubstituted 1,3-dehydroadamantane (X=Y=H) at 54.4δ is split to a doublet in the coupled spectrum and is therefore unambiguously attributed to the bridgehead α carbon (equivalent to the α' carbon). In all cases the quaternary carbons were the weakest signals and the secondary were the strongest. The positions of the several different secondary carbons, β, β', and δ', of 5-cyano-1,3-dehydroadamantane (1 X=CN, Y=H) were also assigned on the basis that substituent effects of a cyano group in 1,3-dehydroadamantane would be similar to those of a cyano group on adamantane.[4] The change in chemical shift, relative to the adamantane compound 2, when the 1,3-cyclopropane bond in present is given in brackets in the Table for each carbon present.

Although cyclopropane carbon chemical shifts are usually found at higher field than in corresponding ring opened compounds[5], in 1,3-dehydroadamantanes the cyclopropyl γ and δ carbons are shifted to lower field by +7 to +9.6 ppm, and +10.2 to +13.6 ppm, respectively. This is similar to the downfield shifts reported in homoadamantanes on introduction of the cyclopropyl bond[2] and, as suggested, may reflect the increased contribution of p-character in these highly strained ring systems. However, the cyclopropyl methylene carbons were split to triplets with coupling constants J_{C-H} of 158 Hz which are normal for a cyclopropanes.[5]

More remarkable are the remote effects of the 1,3-bonding in compounds 1 compared to the parent compounds 2. Both the α and β carbons are shifted to lower field; the bridgehead α carbons by +20 to +29 ppm. A normal inductive effect caused by increased electronegativity of the γ carbons when bonded in a cyclopropyl ring cannot account for the shift being greater at the more remote α carbon than at the adjacent β carbons. Anisotropic shielding effects of the cyclopropane ring, well known in ^{1}H-NMR spectra, are not great enough to give the observed large downfield shifts.[5-7] Any unusual angle strain effects transmitted to the α carbon by the constraints of the inverted carbons at γ positions also do not seem to account for the unusual low field chemical shifts.[8]

The apparently long range effect of the strained cyclopropyl bond in 1 can also be seen in other compounds of closely related geometry. For example, relatively unstrained 2,4-dehydroadamantane (3) shows a very low field signal at 52.5δ (This peak was inadvertently left off the published spectrum of this compound.)[9] This signal is attributed to the δ carbon (see diagram 3) which is a position with respect to the cyclopropyl ring identical to that of the low field bridgehead α carbon in 1,3-dehydroadamantanes (1). No inverted carbons, with associated strain and changes in hybridization, are present in 2,4-dehydroadamantane and they therefore cannot account for the downfield chemical shifts in either 1,3- or 2,4-dehydroadamantanes. Some more specific geometrical factor seems to be involved.

Perhaps there is a through space interaction of π-like orbitals of the cyclopropyl group with the carbon atom situated directly across from the ring (i.e., with the α carbon of 1 and the δ carbon of 3). Thus there may be a relationship between the observed low field chemical shifts reported here and the increased reactivity of groups on such carbon atoms.[10,11]

Table: ^{13}C NMR Chemical Shifts of Dehydroadamantanes[a]

Compound	α	β	β'	γ	δ
1,3-dehydroadamantane	54.4	46.1	37.6	37.3	49.5
1, X = Y = H	(J_{CH} 132Hz)	(J_{CH} 133Hz)			(J_{CH} 158Hz)
Change from adamantane[b]	[+25.9]	[+8.2]	[-0.3]	[+8.8]	[+11.6]
5,7-dimethyl-1,3-dehydroadamantane	59.5	51.0	52.2	36.5	46.4
1, X = Y = CH_3[c]					
Change from adamantyl compound[b]	[+28.9]	[+5.2]	[+1.9]	[+7.0]	[+10.2]
5-cyano-1,3-dehydroadamantane	50.5	49.2	39.8	36.7	49.3
1, X=CN, Y=H[d]		(J_{CH} 135Hz)	(J_{CH} 133Hz)		(J_{CH} 158Hz)
Change from adamantyl compound[b]	[+20.3]	[+9.2]	[-0.2]	[+9.6]	[+13.6]
adamantane	28.5	37.9	37.9	28.5	37.9
2, X = Y = H					
1,3-dimethyladamantane	30.6	43.9	51.8	29.5	36.2
2, X = Y = CH_3[e]					
1-cyanoadamantane	30.2	39.9	39.9	27.0	35.8
2, X=CN, Y=H[f]		(J_{CH} 135Hz)		(J_{CH} 133Hz)	(J_{CH} 128Hz)
2,4-dehydroadamantane[g], 3	20.7	24.1	28.9	32.2	52.5

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[a] Chemical shifts given in δ relative to an internal TMS standard. The solvent used for 1,3-dehydroadamantanes was degassed C_6D_6 since they react rapidly with chloroform and oxygen. Adamantane compounds were determined in $CDCl_3$; the most stable dehydroadamantane compound (the cyano derivative) showed, as expected, no NMR solvent effect between C_6D_6 and $CDCl_3$.

[b] Positive sign indicates a downfield shift.

[c] Methyl groups at 22.5δ.

[d] The α' carbon is at 53.0δ (J_{CH} 132Hz), the δ' carbon is at 44.0δ and the nitrile carbon is at 128δ.

[e] Methyl groups at 31.0δ.

[f] The nitrile carbon has chemical shift 125δ.

[g] The δ' carbon is at 33.4 and the γ' carbon at 26.9δ.

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