

CARBON-13 NMR SPECTRUM OF A NEW HYDROCARBON CONTAINING CARBON ATOMS
WITH "INVERTED" TETRAHEDRAL GEOMETRY ¹

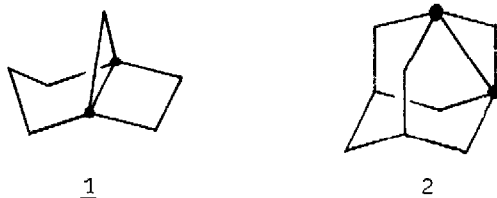
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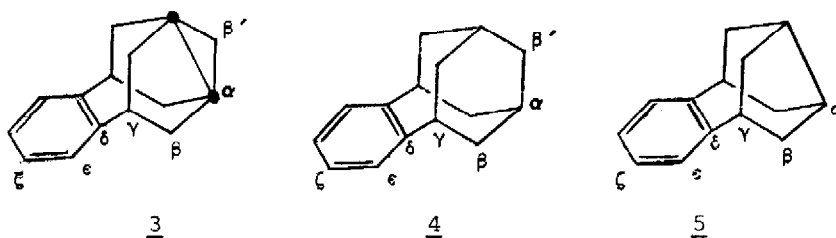
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Recently, hydrocarbon frameworks containing carbons (dots) with "inverted" tetrahedral geometry have been reported, i.e. carbon atoms with all four substituents being in one single hemisphere^{2,3} :



These compounds are of interest because of their reactivity which is different from that of other cyclopropane derivatives. Besides they show unusually large interatomic distances between the two "inverted carbons" (e.g. 1.64 Å in the 5-cyano-derivative of 2³), and their electronic environments seem to be differing remarkably from those of other "normal" cyclopropanes^{4,5,6,7}. Wiberg et al.² as well as Pincock et al.³ assume that the "inverted carbons" are sp² hybrids, the bonds between them being formed by their p orbitals. In the course of investigations of syntheses of several benzohomoadamantane derivatives⁸ the compounds 3, 4, and 5 have been prepared. In this series the



dehydrohomadamantane 3 with two "inverted carbons (α)" was synthesized in a similar way as 1.3-dehydroadamantane³ from the corresponding 1.3-dibromohomadamantane.

Because of the ^1H chemical shift $\delta_{\text{H}} = 1.92$ ppm of the C- β' -protons being remarkably large for protons attached to a three-membered ring (1.66 ppm for the corresponding protons of compound 2³), we were interested in an investigation of the ^{13}C NMR spectra of 3, 4, and 5.

Table: ^{13}C Chemical Shifts of Compounds 3, 4, and 5^a

	α	β	β'	γ	δ	ϵ^c	ζ^c
<u>3</u>	43.5 ₀	45.1 ₀	51.5 ₀	64.5 ₅	145.8 ₅	130.0 ₅	125.7 ₀
<u>4</u>	28.8 ₀	35.6 ₀	36.4 ₀	41.6 ₀	148.1 ₅	128.1 ₀	125.9 ₅
<u>5</u>	42.9 ₀	43.6 ₅	-	49.0 ₀	146.4 ₀	129.2 ₅	125.6 ₅
$\delta_{\underline{3}} - \delta_{\underline{4}}^b$	14.7 ₀	9.5 ₀	15.1 ₀	22.9 ₅	-2.3 ₀	1.9 ₅	-0.2 ₅
$\delta_{\underline{3}} - \delta_{\underline{5}}^b$	0.6 ₀	1.4 ₅	-	15.5 ₅	-0.5 ₅	0.8 ₀	0.0 ₅

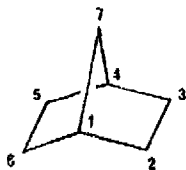
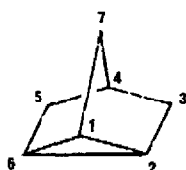
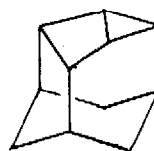
^a In ppm downfield from TMS; solvent: CDCl_3 with TMS as internal standard; accuracy: ± 0.025 ppm.

^b These values are differences between the ^{13}C chemical shifts of corresponding carbons in compounds 3 and 4 and in 3 and 5, respectively.

^c The ϵ and the ζ carbons were assigned using the "fingerprint-rule" for proton-coupled spectra given in ref. 9.

As can be seen from the table the carbons in the three-membered ring in compound 3 are strongly deshielded. This is demonstrated by a comparison of the chemical shifts of 3 and 4:

Formation of a bond between the two α carbons of the homadamantane 4 gives rise to a downfield shift of approximately 15 ppm for the C- α and C- β' signals. An inverse behaviour is expected considering the changes of ^{13}C chemical shifts of alicyclic compounds with decreasing ring size^{10,11} or comparing the chemical shifts of the carbons in question of norbornane 6 and nortricyclene 7¹²:

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In the norbornane framework the formation of a cyclopropane moiety produces an upfield shift of 26.9 ppm for C-1 and of 20.2 ppm for C-2/6. Similarly, Katsushima et al.¹³ reported ¹³C NMR data of pentacyclo[5,3,1,0^{2.6},0^{3.5},0^{4.9}]. undecane 8 including a signal at 7.3 ppm for two tertiary carbons which apparently can be assigned to the two chemically equivalent carbons in the cyclopropane ring. In all these cases, however, no "inverted carbons" are present.

Lippert et al.¹⁴ and Wiberg et al.² calculated hybridization parameters for the atom orbitals of carbons in cyclopropane and reported sp^{2.11} hybrids¹⁴ for hydrogen binding atom orbitals and sp^{4.62}¹⁴ or sp^{4.76} hybrids² for carbon binding atom orbitals. This hybridization pattern differs considerably from the sp² hybridization of "inverted carbons" proposed by Wiberg² and Pincock³. This may explain the different behaviour of the C- α chemical shifts. But this explanation does not hold for the β' -carbon which is deshielded, too, though its coupling constant $|^1J_{CH}| = 155$ Hz is typical for "normal" cyclopropanes.

On the other hand, the shielding of the α carbons (43.5 ppm) is positioned at very high field for a sp² hybridized carbon compared with others in olefinic and aromatic systems. But the p orbital of the "inverted carbon" is not involved in a π -system.

But not only the α and β' carbons show an unexpected behaviour. The "inverted carbons" seem to influence remote carbons, too, e.g. comparing 3 and 4 a downfield shift of nearly 23 ppm is found for the γ signals! Even if a part of this difference is due to the changed geometry of the two frameworks - the α carbons of 3 are closer together than those of 4 - , a comparison of the γ shifts of 3 and the norhomoadamantane 5 with more similar geometry shows a downfield shift of still 15.5₅ ppm which may be attributed to an electronic influence of the three-membered ring with the "inverted carbons" through the σ bonds.

The δ and ϵ shifts of 3 and 4 are differing considerably in spite of the large distance. But in these cases the influence of the changed geometry seems to dominate because the corresponding effects of 3 and 5 are rather small.

The special features of compounds with "inverted carbons" outlined above are to be verified with other systems. Perhaps they are suitable to get further insight into the dependence of ¹³C chemical shifts on the electronic environment.

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