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CARBON-13 CHEMICAL SHIFTS OF INVERTED CARBON ATOMS

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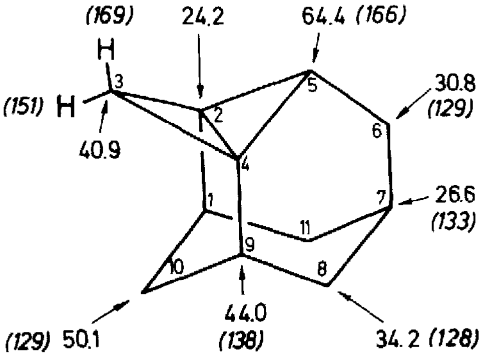
Summary: The inverted carbons in 2,4-methano-2,4-dehydroadamantane are shielded by 14.3 ppm relative to the corresponding carbons in 2,4-methanoadamantane. This was explained by the balance of the inverted carbon hybridization deshielding, the shielding effect of the cyclopropane rings formed, and the change in the influence of the neighbouring atoms.

Inverted carbon atoms[1] (carbons with inverted tetrahedral geometry) were reported to be "strongly deshielded" relative to the corresponding carbons in the respective ring-opened compounds.[2,3] This was suggested to reflect the "sp^2 hybridization" of the inverted carbons, the "free" orbitals of which are not involved in a π-system but overlap each other to make a p-p σ bond.[2,3]

We wish to report the shielding of the inverted carbons in 2,4-methano-2,4-dehydroadamantane (**1**) relative to the corresponding carbon atoms in 2,4-methanoadamantane (**2**). Hydrocarbon **1** is a derivative of [3.1.1]propellane, which is the smallest carbocyclic ring propellane system that has been reported.[4,5] It was obtained by intramolecular cycloaddition of 4-methylene-2-adamantylidene generated by pyrolysis of the dry sodium salt of 4-methylene-2-adamantanone tosylhydrazone.[4] Compound **2** was prepared by addition of thiophenol to **1** followed by Raney nickel desulfurization of the resulting 2-thiophenyl-2,4-methanoadamantane.[4] Hydrocarbons **1**[4] and **2**[6] were identified by C-13 and H-1 NMR, IR, and mass spectrometry.



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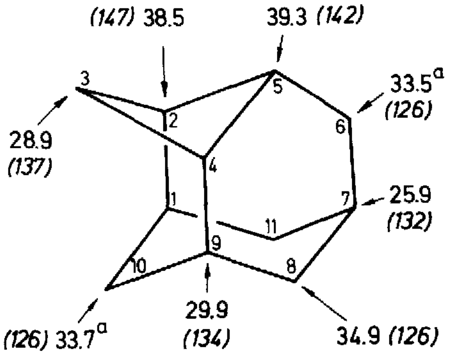

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C-13 NMR Chemical shifts in ppm (relative to internal TMS, accuracy: ±0.1 ppm) and one-bond C-H coupling constants in Hz (values in parentheses, accuracy: ±2 Hz for **1** and ±3 Hz for **2**). [a] The assignements are uncertain and can be reversed.

Carbon-13 NMR spectra of **1** and **2** were recorded with a JEOL FX-100 spectrometer from C_6D_6 solutions under a dry nitrogen atmosphere.[7] All signals, except those corresponding to carbons 6 *and 10 in* **1**, *and 6 and 10 in* **2**, *were assigned by the quantitative and off-resonance decoupled spectra*, as well as by the C-H coupling constants. The assignment of the C-3 signal in **1** was confirmed by deuterium labelling at this carbon.[8] The signals of C-6 and C-10 in **1** were distinguished using the successive selective decoupling technique.[9]

The signal of the inverted carbon atoms (2,4) in **1** is shifted upfield by 14.3 ppm relative to that of the corresponding carbons (2,4) in **2**. This upfield shift is apparently inconsistent with the relative downfield shifts reported previously for the inverted carbons in 4,5-benzo-1,8-dehydrohomoadamantane[2] *and for a series of 5-substituted 1,3-dehydroadamantanes.*[3] *However, the chemical shift of* an inverted carbon, compared to that of the corresponding carbon in the respective ring-opened compound, should depend on the balance of the three major factors: the deshielding owing to the carbon rehybridization, the shielding effect of the new rings formed, and the change in the influence of the neighbouring atoms caused by the formation of the new bond. The latter may reasonably be expected to result in a weak or moderate deshielding effect. In the case of **1** the strong shielding effect of the two cyclopropane rings prevails over the deshielding effect of both the inverted carbons and the neighbouring atoms. *The influence of a single cyclopropane ring presumably cannot overcome this deshielding.* Consequently, the net deshielding effect of the inverted carbon hybridization appears to be stronger than the apparent effects reported previously.[2,3]

Carbon 10 in **1** is strongly deshielded compared to the corresponding carbon (10) in **2**. This is in good agreement with the relative deshieldings of the carbon atom situated across from the cyclopropane ring observed in other bicyclo[3.1.0]hexanes in the chair conformation.[2,3,10] The relative deshieldings of this carbon in **1** and 2,4-dehydroadamantane[3] are comparable, 16.5 and 14.6 ppm, respectively, indicating that the influence of the other, syn cyclopropane ring is considerably smaller. Hence, these interactions depend strongly on the sterical arrangement.[11] The both cyclopropane rings in **1**, anti and syn, display the deshielding effect at C-10. However, when the syn cyclopropane ring is not a part of the bicyclobutane moiety the corresponding carbon is generally shielded.[10]

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References and Notes

1. Carbon atoms with all four bonds directed to a single hemisphere.
2. H. Duddeck and H. Klein, Tetrahedron Letters, 1917 (1976).
3. R.E. Pincock and Fu-Ning Fung, Tetrahedron Letters, 19 (1980).
4. K. Mlinarić-Majerski and Z. Majerski, J. Am. Chem. Soc., 102, 1418 (1980), and unpublished results.
5. Very recently G. Szeimies obtained another carbocyclic derivative of [3.1.1]propellane (private communication). A heterocyclic [3.1.1] propellane derivative was reported previously: U. Szeimies-Seebach, G. Szeimies, M. Van Meerssche, G. Germain, and J.-P. Declercq, Nouv. J. Chim., 3, 357 (1979).
6. T. Sasaki, S. Eguchi, and Y. Hirako, J. Org. Chem., 42, 2981 (1977).
7. Propellane **1** reacts rapidly with oxygen.[4]
8. 2,4-Methano-3,3-d_2-2,4-dehydroadamantane was prepared from the sodium salt of 4-methylene-d_2-adamantanone tosylhydrazone.[4]
9. See L.F. Johnson in "Topics in Carbon-13 NMR Spectroscopy", Vol. 3, G.C. Levy, Ed., Wiley-Interscience, New York, 1979, p 7. Since the two hydrogen atoms on C-10 are nonequivalent, the C-10 signal was changing, depending on the decoupling frequency applied, from a doublet of doublets through a doublet, then a singlet, and another doublet to a final doublet of doublets. The two hydrogens on C-6 are equivalent and, consequently, the signal of this carbon was changing from a triplet through a singlet to another triplet.
10. M. Christl and R. Herbert, Org. Magn. Reson., 12, 150 (1979).
11. The deshielding effect is considerably less pronounced for 2,4-dehydronoradamantane in which the chair conformation of the bicyclo[3.1.0] hexane ring system is distorted. C-13 NMR ($CDCl_3$): 2,4-dehydronoradamantane δ 47.4 (t, $J=128$ Hz, 3C), 40.7 (d, $J=137$ Hz, 3C), and 37.5 (d, $J=171$ Hz, 3C), noradamantane δ 44.2 (t, 4C), 37.6 (d, 2C), 36.8 (d, 2C), and 35.7 (t, 1C).

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