^{13}C Nuclear Magnetic Resonance Spectra. Part 9.[1] Strain Effects on ^{13}C Chemical Shifts of Triamantane

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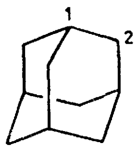
The ^{13}C n.m.r. spectrum of triamantane (3) observed at 22.64 and 62.8 MHz is assigned using selective ^1H decoupling. Internal strain causing geometrical distortions at the quaternary carbon leads to a non-additive downfield shift of its signal.

In the course of our investigations on the chemical and spectroscopic properties of substituted and unsubstituted diamondoid hydrocarbons we have made a detailed ^{13}C n.m.r. study of triamantane [2] (3). Triamantane is a $C_{18}H_{24}$ hydrocarbon composed of three fused adamantane subunits and has C_{2v} symmetry. Thus the molecule shows eight different types of carbon sites.



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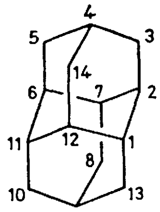

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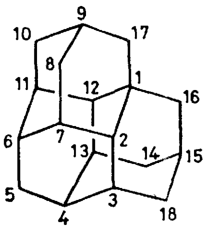

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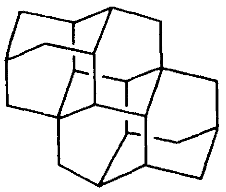


(4)

RESULTS

In Table 1 the ^{13}C chemical shifts of triamantane (3) at 22.64 (column I) and 62.8 MHz (column II) are listed.

Table 1

Observed and calculated ^{13}C chemical shifts (relative to $SiMe_4$) of triamantane

	Observed		Calculated	
Carbons	I [a]	II [b]	III [c]	IV [d]
1	33.6	33.87	27.9	37.6
2, 12	46.9	47.10	44.1	46.9
3, 7, 11, 13	38.1	38.30	34.7	38.3
4, 6	35.3	35.43	34.7	35.2
5	38.6	38.72	35.0	39.0
8, 10, 14, 18	38.1	38.26	35.0	35.9
9, 15	27.8	27.96	25.2	26.6
16, 17	45.3	45.50	44.5	47.6

[a] Recorded in deuteriochloroform at 22.64 MHz using a Bruker WH-90 spectrometer. [b] Recorded at 62.8 MHz using a CAMECA 250 spectrometer. [c] Calculated using Beierbeck and Saunders' parameter set.[10] [d] Calculated using the additivity rule described in the text.

The peak assignments were achieved as follows. The relative intensities of the signals were determined as 2 : 2 : 1 : 8 : 2 : 1 : 2 from lower to higher field. In order to suppress the nuclear Overhauser effect the protons were broad band decoupled only during the acquisition of the f.i.d. with 10 s delay between two pulses; the flip angle was *ca.* 30°. With the help of an off-resonance spectrum, an unambiguous assignment of the signals at δ 45.3, 38.6, 38.1, and 33.6 p.p.m. is possible (*cf.* Table 1). That at δ 38.1 p.p.m. consists of two coinciding signals, each representing four chemically equivalent carbon atoms. At 62.8 MHz it is split into two signals at δ 38.30 and 38.26 p.p.m.; their assignment follows from the off-resonance spectrum.

Even with the long delay of 10 s between the pulses the signal of the quaternary carbon atom C-1 at δ 33.6 p.p.m. is very weak indicating a long longitudinal relaxation time for this atom.

The 250 MHz ^1H n.m.r. spectrum of (3) does not differ significantly from that at 100 MHz reported earlier.[2] Except for the protons attached to C-16 and -17, C-2 and -12, and C-9 and -15 at δ 1.24, 1.40, and 1.82, respectively, all signal positions are very close to δ 1.65, and the higher field does not allow a better understanding of these latter signals.

Among selective ^1H decoupling experiments only the one irradiating the protons attached to C-9 and -15 at δ 1.82 could be used for an unambiguous assignment of the three methine signals at δ 47.10, 35.43, and 27.96 p.p.m., each representing two carbons: the signal at δ 27.96 p.p.m. only gave a singlet; it was thus attributed to C-9 and -15. The two others appeared as doublets with a residual coupling smaller for that at δ 47.10 and larger for that at 35.43 p.p.m. As the residual coupling J_r depends on the difference between the frequency of irradiation and the resonance frequency of the proton(s) concerned [3] these J_r values could be used to attribute these signals to C-2 and -12 and C-4 and -6, respectively.

This assignment of the ^{13}C signals is supported by additivity calculations so that the ^1H signal assignment given by Schleyer *et al.*[2] is probably correct, also in cases where it may not have been absolutely unambiguous.

DISCUSSION

It is now known that diamondoid hydrocarbons are not the strain-free molecules which they were considered earlier due to their assumed tetrahedral geometry. The strain energy of adamantane (1) is 25—29 kJ mol^{-1} which is believed to be caused by C–C and H–H nonbonding repulsions;[4,5] those of diamantane[4,6] (2) and triamantane[4] (3) are presently estimated to be *ca.* 45—50 and 56.5 kJ mol^{-1}, respectively. The published *X*-ray analysis of triamantane[7] confirms the structure but no bond angles and lengths are given. However, a recent *X*-ray study of tetramantane[8] (4) showed that the bond lengths increase with decreasing number of hydrogen atoms at the bonded carbon atoms. Furthermore, considerable changes of the bond angles are observed, particularly at the quaternary carbons. Here the CH_2-C-CH_2 bond angle is 111.8° and that between the two CH–C bonds 107.4°, whereas the other C–C–C bond angles are mostly in the range 109—111°. Such extraordinary bond angle distortions have not been found at diamantane[9] (2), but they must be expected to exist also at C-1 (quaternary) of triamantane (3). Since ^{13}C n.m.r. spectroscopy is a sensitive probe of the electronic environment of carbon atoms, the molecular strain in triamantane (3) resulting in such alterations of bond lengths and bond angles is reflected in its ^{13}C n.m.r. spectrum.

Recently Beierbeck and Saunders[10] introduced a semiempirical procedure to calculate ^{13}C chemical shifts of saturated hydrocarbons in staggered conformations. Their parameter set is based on β- and γ-C–C and -C–H interactions and was derived from a large number of fused ring systems such a decalins, steroids, and triterpenes by regression analysis. It turned out that this parameter set is not well suited to the prediction of the chemical shifts of diamondoid hydrocarbons (*cf.* Table 2 and Table 1, column III) exactly.

TABLE 2

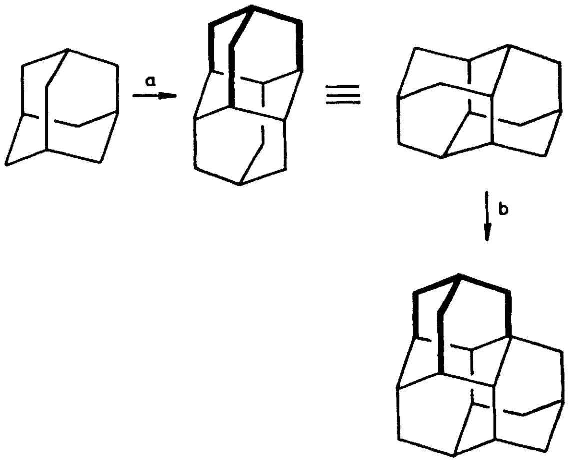
Observed[a] and calculated[b] ^{13}C chemical shifts (relative to $SiMe_4$) of adamantane (1) and diamantane (2)

		^{13}C Chemical shifts	
Molecule	Carbon	Observed	Calculated
(1)	1	28.5	25.2
(1)	2	37.8	35.0
(2)	1	37.7	34.7
(2)	3	38.4	35.0
(2)	4	26.9	25.2

[a] Similar chemical shifts were reported by T. M. Gund, E. Osawa, V. Z. Williams, jun., and P. v. R. Schleyer, *J. Org. Chem.*, 1974, **39**, 2979. [b] The chemical shifts are calculated using Beierbeck and Saunders' parameter set.[10]

All predicted chemical shifts are too small, generally by *ca.* 3 p.p.m. This is not surprising, since the parameters[10] have been computed using values from cyclohexyl systems in which the cyclohexane ring is known to be somewhat flattened[11,12] compared with the geometry implied by molecular models with their ideal tetrahedral bond angles. This is not true to the same extent for diamondoid hydrocarbons[9,13] and, apparently, these small geometrical differences are the reason for the inaccuracies in the calculations above.

We therefore present an alternative prediction of the ^{13}C chemical shifts of triamantane (3) (Scheme). The diamantane framework can be considered to be formed by addition of an isobutane unit to the adamantane skeleton (*cf.* Scheme a). This leads to the following increments of the chemical shifts of the former adamantane carbon atoms: α (C-1, -7, -11) −0.1, β (C-2, -6, -12) +9.2, γ (C-3, -5, -14) +0.6, and δ (C-4) −2.5 p.p.m. It should be noted that these increments differ remarkably from those expected using known additivity rules.[14] Analogously, the triamantane molecule may be constructed by attaching an isobutane unit to the diamantane framework (*cf.* Scheme b). Adding the increments to the diamantane chemical shifts in the appropriate manner one obtains calculated chemical shifts which correspond to a hypothetic triamantane skeleton whose carbon shifts contain no essential contribution from geometrical distortion which were not known before. These calculations only concern the carbon atoms of the central adamantane unit; the signals of C-8, -10, -14, -18, C-9, -15, and C-16, -17 can only be estimated, and thus their agreement with the observed values is rather poor. The chemical shifts of the central adamantane unit, however, correspond excellently with those observed except for C-1. The bond angle distortions lead to a 4 p.p.m. downfield shift of its ^{13}C signal. This non-additive contribution to the C-1 chemical shift must be regarded as a consequence of additional internal strain in the triamantane molecule caused by pairwise non-bonded repulsion of the hydrogens at C-16 and -17.[8]



SCHEME

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