

**$^{29}\text{Si}$  AND  $^{13}\text{C}$ -NMR SPECTRA AND STERIC EFFECTS IN MONO- AND BIS(TRIMETHYLSILOXY)ADAMANTANES\***

Jan SCHRAML<sup>a</sup>, Jaroslav VČELÁK<sup>a</sup>, Václav CHVALOVSKÝ<sup>a</sup>, Günter ENGELHARDT<sup>b</sup>, Harald JANCKE<sup>b</sup>, Luděk VODIČKA<sup>c</sup> and Josef HLA VATÝ<sup>c</sup>

<sup>a</sup>*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague - Suchbøl,*

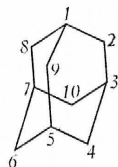
<sup>b</sup>*Central Institute of Physical Chemistry, Academy of Sciences of GDR, 1199 Berlin - Adlershof, GDR and*

<sup>c</sup>*Laboratory of Synthetic Fuels, Prague Institute of Chemical Technology, 166 28 Prague 6*

Received February 2nd, 1978

The  $^{29}\text{Si}$ - and  $^{13}\text{C}$ -NMR spectra of several mono- and bis(trimethylsiloxy)substituted adamantanes are described. The assignment of the lines in the spectra to individual nuclei in the molecules is based on symmetry and intensity considerations, off-resonance proton decoupling experiments and additivity rules. The number of isomeric bis(trimethylsiloxy)adamantanes and the number of nonequivalent adamantane skeleton carbon atoms permitted the establishment of the validity of the additivity rules and of the shielding contributions including those dependent on the steric factors. The silicon chemical shifts in 1-adamantyl and 2-adamantyl derivatives are found in two distinctly different spectral regions and it is suggested that the silicon chemical shifts together with the skeleton carbon shifts can be used to complete structure determination of any adamantane derivative after its conversion into the corresponding trimethylsiloxy derivative. The silicon chemical shifts show sensitivity to steric interaction; intramolecular crowding leading in adamantane derivatives to diamagnetic steric silicon shifts. Multiple substitution of the adamantane results in large deviations from additivity for the substituted adamantane skeleton carbon atoms if the substituents are close enough to interact sterically. Since such interactions are not accompanied by chemical shift changes of the methyl carbon atoms an ambiguity exist about the origin of the steric effects.

In connection with our studies of steric effects in NMR spectra of trimethylsilyl and trimethylsiloxy derivatives<sup>1-4</sup> and the application of  $^{29}\text{Si}$ -NMR to structure determination of organic compounds<sup>5-6</sup> we have investigated  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra of several mono- and bis(trimethylsiloxy)substituted adamantanes. The results of this investigation are presented here. In all the following text the adamantane carbon atoms are numbered according to IUPAC rules as shown on Scheme 1.



SCHEME 1

\* Part CLVII: in the series Organosilicon Compounds; Part CLVI: This Journal 43, 753 (1978).

## EXPERIMENTAL

## Materials

The purity of all hydroxyadamantanes was checked by gas chromatography and their identity proved by mass and  $^1\text{H-NMR}$  spectra (the latter measured in the presence of shift reagents<sup>7-9</sup>). In order to avoid confusion, the substituent position in configuration isomers are denoted here by capital superscripts *E* and *A* (equatorial and axial, resp.). 1-Hydroxyadamantane was prepared by a reaction of adamantane with bromine in nitric acid<sup>10</sup>. After recrystallization from cyclohexane and resublimation (140°C/15 Torr) the product melting at 282–283°C (in a sealed capillary) was obtained (reported m.p. 288.5–290°C (ref.<sup>11</sup>) and 282°C (ref.<sup>12</sup>)). For  $\text{C}_{10}\text{H}_{16}\text{O}$  (152.2) calculated: 78.90% C; 10.59% H; found: 79.03% C; 10.70% H. 2-Hydroxyadamantane was prepared by the  $\text{LiAlH}_4$  reduction of adamantanone in dry ether<sup>13</sup>. The product melting at 296.3–297.9°C (in a sealed capillary) was isolated by recrystallization from cyclohexane and resublimation (130°C/15 Torr) (lit.<sup>13</sup> m.p. 296.2–297.2°C). For  $\text{C}_{10}\text{H}_{16}\text{O}$  (152.2) calculated: 78.90% C; 10.59% H; found: 78.76% C; 10.67% H.

1,2-Dihydroxyadamantane was prepared from 4-protoadamantanone according to the procedure described in literature<sup>14</sup>. The purification of the product included chromatography on a silica gel column, crystallization from methyl ethyl ketone and sublimation (220°C/15 Torr). It afforded pure 1,2-dihydroxyadamantane melting in a sealed capillary at 326–327°C (lit.<sup>14</sup> m.p. 326 to 330°C). For  $\text{C}_{10}\text{H}_{16}\text{O}_2$  (168.2) calculated: 71.39% C; 9.59% H; found: 71.30% C; 9.51% H.

1,3-Dihydroxyadamantane was obtained by disproportionation of 1-hydroxyadamantane in 70%  $\text{H}_2\text{SO}_4$  as described in literature<sup>15</sup>. Crystallization from ethyl acetate–ethanol (9:1) mixture and sublimation (190°C/15 Torr) gave a crystalline compound melting at 333–334°C (lit.<sup>15</sup> m.p. 325–330°C). For  $\text{C}_{10}\text{H}_{16}\text{O}_2$  (168.2) calculated: 71.39% C; 9.59% H; found: 71.33% C; 9.55% H.

1,4-Dihydroxyadamantanes and 2,4-dihydroxyadamantanes were prepared and purified as described elsewhere<sup>16</sup>, their  $^{13}\text{C-NMR}$  spectra are presented in this issue<sup>17</sup>.

2,6-Dihydroxyadamantane was prepared by the  $\text{LiAlH}_4$  reduction<sup>18</sup> in a dry ether in 93.5% yield. Crystallization from ethyl acetate and sublimation (200°C/15 Torr) provided a white crystalline compound with m.p. 344–345°C (lit.<sup>18,19</sup> m.p. 344°C). For  $\text{C}_{10}\text{H}_{16}\text{O}_2$  (168.2) calculated: 71.36% C; 9.58% H; found: 71.27% C; 9.54% H.

*1-Trimethylsilyoxyadamantane* (I). 1-Hydroxyadamantane (1.5 g) was silylated by an excess of a 1:1 molar mixture of trimethylchlorosilane and hexamethyldisilazane (3.2 g) in the absence of any solvent. The reaction mixture was stirred and gradually heated to its boiling point for 5 hours. At the beginning of the reaction the mixture became homogeneous. The fractions boiling below 160°C were distilled off and the residue was vacuum distilled. The isolated fraction (b.p. 117°C/11 Torr), m.p. 32°C; lit.<sup>20</sup> b.p. 118–119°C/11 Torr, m.p. 30–31.5°C) contained no starting adamantanol, as proved by gas chromatography of an acetone solution. The yield was 2.0 g (92%), all the losses occurring through the isolation process.

*2-Trimethylsilyoxyadamantane* (II) was prepared analogously to compound *I* from 0.5 g of 2-hydroxyadamantane and a fivefold excess of the silylating mixture. The reaction mixture homogenizes gradually in the course of the reaction. Vacuum distillation yielded 0.6 g of the product ( $n_D^{20}$  1.4790) which was pure according to gas chromatography.

*1,2-Bis(trimethylsilyoxy)adamantane* (III) was prepared in 40% yield by silylation in pyridine.

*1,3-Bis(trimethylsilyoxy)adamantane* (IV). Several approaches to the silylation of 1,3-dihydroxyadamantane were tried. A tenfold excess of the silylating agent consisting of trimethylchloro-

silane and hexamethyldisilazane converts only 10% of the diol into mono(trimethylsiloxy) derivative after 9 hours reflux. Further silylation in the presence of dioxane (which partially dissolves the diol) gives, after 10 hours of reflux, 80% conversion into the mono derivative. Repeated silylation of the product of the above silylation by 15-fold excess of the silylating reagent in dioxane gave a mixture of 87% bis- and 13% monosilylated derivatives. The mixture (0.22 g) was refluxed again with 1.8 g of the silylating reagent in 2 ml of pyridine for 5 hours. The homogeneous mixture was then vacuum distilled and 0.21 g (92%) of liquid 1,3-bis(trimethylsiloxy)adamantane ( $n_D^{20}$  1.4698) was obtained chromatographically pure.

1,4<sup>E</sup>-Bis(trimethylsiloxy)adamantane (V) was prepared by the silylation of the corresponding diol (0.25 g) by a 10-fold excess of the silylating reagent (trimethylchlorosilane and hexamethyldisilazane 1 : 1 mol) in 2 ml of pyridine. After 20 hours the solvent was distilled off and the product was vacuum distilled (0.44 g, 90% yield), ( $n_D^{20}$  1.4672).

1,4<sup>A</sup>-Bis(trimethylsiloxy)adamantane (VI) was prepared in 80% yield by an analogous procedure as the 1,4<sup>E</sup> isomer.

2<sup>E</sup>,4<sup>E</sup>-Bis(trimethylsiloxy)adamantane (VII) was prepared by the same procedure. The starting diol which is insoluble in pyridine gradually dissolved in the course of the reaction, the isolated liquid product was obtained in 64% yield.

2<sup>A</sup>,4<sup>E</sup>-Bis(trimethylsiloxy)adamantane (VIII) was obtained in 96% yield by the same procedure from 0.15 g of the corresponding diol.

2<sup>A</sup>,4<sup>A</sup>-Bis(trimethylsiloxy)adamantane (IX) was obtained by the same procedure in 82% yield from 0.22 g of the corresponding diol.

2,6-Bis(trimethylsiloxy)adamantane (X) was also prepared (in 36% yield) by the above silylation in pyridine. Vacuum distillation gave the solid product, which after purification by sublimation had m.p. 73°C.

### Spectra

<sup>29</sup>Si- and <sup>13</sup>C-NMR spectra were measured on a JEOL-PFT-100 spectrometer interfaced to a Nicolet 1085 data system. Both spectra were measured in the FT mode (using 8k for FID) in tetrachloromethane solutions (the concentration varied from 5 to 50% according to the availability and solubility of the compound) which contained a few drops of hexamethyldisiloxane. <sup>29</sup>Si-NMR spectra were (in 2 kHz range) recorded at 19.87 MHz while the spectrometer was locked to <sup>19</sup>F signal of CF<sub>3</sub>COOH placed in a capillary. The spectra were proton gated decoupled (to suppress the negative Overhauser effect) and the chemical shifts were referenced to the line of internal hexamethyldisiloxane ( $\delta = 6.66$ ). <sup>13</sup>C-NMR spectra in 5 kHz range were recorded at 25.14 MHz. The spectrometer was locked to <sup>2</sup>H line of C<sub>6</sub>D<sub>6</sub> in a capillary, protons were noise decoupled. The chemical shifts were referenced to carbon tetrachloromethane line ( $\delta = 95.98$ ).

## RESULTS AND DISCUSSION

### <sup>29</sup>Si-NMR Chemical Shifts

The silicon-29 chemical shifts observed in the studied adamantane derivatives are collected in Table I. The shifts fall into two distinct ranges of  $\delta$  values: 6.1–7.1 and 11.1–13.7. Based on the shifts in the two mono trimethylsiloxyadamantanes a con-

sistent assignment of the shifts in all the disubstituted isomers is achieved. The first range of the shifts is assigned to the silicon nucleus Si(t) of the trimethylsiloxy group on the tertiary (methine) carbon atom of the adamantane while in the second range the signals of Si(s) from the group bonded to a secondary (methylene) carbon atom appear. The two ranges in the adamantane derivatives are in agreement with the general observation of an approximate 3 ppm upfield steric shift caused by the  $\gamma$ -gauche methyl (or CH) group<sup>4</sup> and the values are in accord with the shifts observed in isopropoxy- and tert-butoxytrimethylsilanes. The persistence of the marked shift difference between the two types of trimethylsiloxy groups in bis(trimethylsiloxy)-adamantanes can be of an analytical use.

In bis(trimethylsiloxy)adamantanes the second trimethylsiloxy group shifts the silicon resonance to a low-field relative to the mono substituted compounds; the only exception being 2<sup>A</sup>,4<sup>A</sup>-bis(trimethylsiloxy)adamantane which will be discussed later in detail. Such a paramagnetic substituent shift is in accord with the effects expected from the electron-withdrawing groups. The effects (in parentheses in Table I) observed on Si(s) nuclei are always larger (by 20–50%) than those observed on Si(t) nuclei. (There is, however, an apparent linear relationship between Si(s) and Si(t) chemical shifts.)

TABLE I  
<sup>29</sup>Si NMR Chemical Shifts of Trimethylsiloxy-substituted Adamantanes<sup>a</sup>

Substitution <sup>b</sup>	$\delta(\text{Si}(t))^{c,d}$	$\delta(\text{Si}(s))^{c,d}$
1-(M)	6.18 (0.00)	—
2-(M)	—	12.58 (0.00)
1,2-(M) <sub>2</sub>	7.05 (0.87)	13.62 (1.04)
1,3-(M) <sub>2</sub>	7.03 (0.85)	—
1,4 <sup>E</sup> -(M) <sub>2</sub>	6.66 <sup>e</sup> (0.48)	13.28 (0.70)
1,4 <sup>A</sup> -(M) <sub>2</sub>	6.46 (0.28)	13.13 (0.55)
2 <sup>E</sup> ,4 <sup>E</sup> -(M) <sub>2</sub>	—	13.23 (0.65)
2 <sup>A</sup> ,4 <sup>E</sup> -(M) <sub>2</sub> <sup>f</sup>	—	13.31 (0.73)
		13.14 (0.56)
2 <sup>A</sup> ,4 <sup>A</sup> -(M) <sub>2</sub>	—	11.16 (−1.42)
2,6-(M) <sub>2</sub>	—	12.76 (0.18)

<sup>a</sup> The shifts are on  $\delta$  scale (relative to (CH<sub>3</sub>)<sub>4</sub>Si line, paramagnetic shifts positive). <sup>b</sup> (M) denotes trimethylsiloxy ((CH<sub>3</sub>)<sub>3</sub>SiO) group, <sup>E</sup> and <sup>A</sup> denote equatorial and axial position of the substituent, resp. <sup>c</sup> The indices in parentheses indicate to which adamantane carbon atom is the (M) group attached, (t) to tertiary or bridgehead carbon atom and (s) to secondary or bridge carbon atom. <sup>d</sup> The values in parentheses are SCS values, *i.e.* the shifts relative to the monosubstituted adamantanes. <sup>e</sup> The line coincided with the reference. <sup>f</sup> The lines could not be assigned.



The difference in the silicon Si(t) shifts and silicon substituent shifts between the crowding-free 1,4<sup>E</sup>- and 1,3-isomers is in full agreement with the known dependence of the silicon chemical shift on polar  $\sigma^*$  constants<sup>21,22</sup> and with the dependence of these constants on the length of the alkyl chain<sup>23,24</sup>. Also, the Si(s) silicon shift in the 2,6-isomer (which is also crowding-free and in which the substituents are most remote) is, in agreement with these dependences, shifted only by 0.18 ppm downfield relative to 2-trimethylsiloxyadamantane.

Slightly different silicon Si(t) and Si(s) chemical shifts in 1,4-isomers indicate that the geometry factors play also some role in determining the chemical shift of the silicon. Since no crowding of the substituent groups is possible in the 1,4<sup>E</sup>-isomer and since the inductive influences in both isomers should be the same, the 0.1 to 0.2 ppm shift difference can be assigned to the diamagnetic steric shifts in 1,4<sup>A</sup>-bis(trimethylsiloxy)adamantane.

In the 1,2-isomer a large downfield shift caused by the inductive effect of the  $\beta$ -trimethylsiloxy group is compensated by a relatively large diamagnetic steric shifts. The steric shifts are, however, different for the two silicon atoms.

Along the lines of thoughts of ref.<sup>4</sup> and according to molecular models, Si(t) silicon in 1-trimethylsiloxyadamantane is at all values of the Si—O—C—C dihedral angles subject to steric interactions with some of the six methylene hydrogen atoms, and, hence the second substituent in 1,2-isomer replaces only one of the six interacting atoms by the bulkier group. In contrast, in 2-trimethylsiloxyadamantane the Si(s) silicon atom is subject to steric interaction only in a limited interval of the dihedral angle values. Substitution at the C—1 bridgehead position not only replaces one of only two sterically interacting hydrogen atoms but leaves almost no space for the trimethylsiloxy group without steric interactions (either with the C—1 substituent or with the adamantane hydrogen atoms). (Accordingly, the diamagnetic steric shifts are estimated on the basis of correlations<sup>21,22</sup> to be approximately 1.4 and 2.9 ppm for Si(t) and Si(s) silicons, resp., in the 1,2-isomer).

In the 2,4-isomers, the inductive influences are similar as in the 1,3-isomer and hence one would expect shifts in the vicinity of  $\delta(\text{Si(s)}) = 13.5$ . The shifts found in the 2<sup>E</sup>,4<sup>E</sup>- and 2<sup>A</sup>,4<sup>E</sup>-isomers are somewhat more diamagnetic but the shift in the crowded 2<sup>A</sup>,4<sup>A</sup>-isomer is more diamagnetic by about 2.3 ppm. This diamagnetic shift is obviously due to the steric effects. The above estimates of steric shifts should be considered as very approximate but their diamagnetic nature is beyond any doubts.

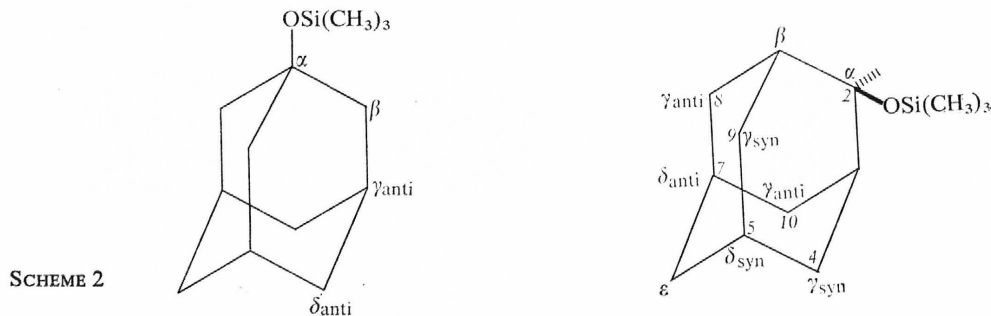
### <sup>13</sup>C-NMR Chemical Shifts

Adamantane skeleton carbon lines were assigned first on the basis of symmetry and intensity considerations combined with off-resonance proton decoupling experiments. Then, the remaining assignment problems in monosubstituted adamantanes were solved according to the analogy with the assigned spectra of hydroxyda-

adamantanes which are very similar. For 1-hydroxyadamantane the spectral assignments given in refs<sup>25-27</sup> were used while for 2-hydroxyadamantane the results of other studies<sup>28,29</sup> were employed. In the spectra of bis(trimethylsiloxy)adamantanes the lines of the same intensity and multiplicity were assigned according to the additivity rules. The lines which were assigned to the skeleton carbon atoms without any use of additivity rule are marked out in Table II in which all the carbon chemical shifts are summarized. In assigning the methyl carbon lines to different trimethylsiloxy groups in disubstituted adamantanes the shift pattern set by the monosubstituted compounds was followed. The line occurring in some of the spectra around  $\delta = 1.9$  was assigned to an impurity.

*Substituent effects and additivity rule.* Pehk, Lippmaa and coworkers<sup>26</sup> noted that the carbon chemical shifts in unsubstituted adamantane calculated from additive parameters of Grant and Paul<sup>30</sup> agree quite well with the experiment. Substituent chemical shifts have been derived from the shifts in monosubstituted adamantanes for a number of adamantane substituents<sup>25-29,31</sup>, but the additivity of the effects of substituents on adamantane skeleton has been verified only in a few instances (1,3-disubstituted adamantanes<sup>26</sup>, 1,3-di-, 1,3,5-tri-, and 1,3,5,7-tetrahaloadamantanes<sup>31</sup>) in which a direct steric interaction between the substituents was impossible. In geminally disubstituted adamantanes a co-operation of the substituents was, however, reported<sup>32</sup>.

Using the assigned carbon chemical shifts in adamantane, 1-trimethylsiloxyadamantane, and 2-trimethylsiloxyadamantane (Table II) the substituent chemical shifts (SCS) of the trimethylsiloxy groups (on secondary and tertiary carbon atoms) given in Table III were derived. The substituent effects were labelled according to the Scheme 2. (Though in the 1-derivative no  $\gamma_{\text{syn}}$  and  $\delta_{\text{syn}}$  carbon atoms are present, the  $\gamma$  and  $\delta$  carbon atoms are labelled  $\gamma_{\text{anti}}$  and  $\delta_{\text{anti}}$  to stress the same spatial relationships as have the *anti* carbon atoms in the 2-derivative.)



The carbon chemical shifts calculated from the substituent chemical shifts for bis(trimethylsiloxy)adamantanes in which nonbonding interactions between the two

TABLE II

 $^{13}\text{C}$ -NMR Chemical Shifts  $\delta$  and Deviations  $\Delta$  from Additivity Rules in Trimethylsiloxy-substituted Adamantanes<sup>a</sup>

Substitution <sup>b</sup>	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	RMS	CH <sub>3</sub> (s) <sup>c</sup>	CH <sub>3</sub> (t) <sup>c</sup>
—	28.07	37.59											
1-(M)	70.74	46.08	30.80	36.28	30.80	36.28	30.80	46.08	46.08	36.28		—	2.84
2-(M)	35.16	74.67	35.16	31.04	27.49	37.69	27.11	36.52	31.04	36.52		0.03	—
1,2-(M) <sub>2</sub> <sup>d</sup>	73.21 <sup>e</sup> (-4.62)	78.55 <sup>e</sup> (-4.61)	37.54 (-0.35)	29.87 (0.14)	29.87 (-0.35)	36.52 (0.14)	30.30 (0.46)	45.06 (0.05)	38.90 (-0.63)	35.69 (0.48)	0.66	0.55	2.98
1,3-(M) <sub>2</sub>	72.83 <sup>e</sup> (-0.64)	54.24 (-0.33)	72.83 <sup>e</sup> (-0.64)	44.73 <sup>e</sup> (-0.04)	31.13 <sup>e</sup> (-2.40)	34.87 (-0.10)	31.13 <sup>e</sup> (-2.40)	44.73 <sup>e</sup> (-0.04)	44.73 <sup>e</sup> (-0.04)	44.73 <sup>e</sup> (-0.04)	0.35	—	2.84
1,4 <sup>E</sup> -(M) <sub>2</sub>	70.25 <sup>e</sup> (0.47)	44.37 (-0.64)	37.03 <sup>e</sup> (-0.50)	73.73 <sup>e</sup> (0.37)	37.03 <sup>e</sup> (-0.86)	29.81 (0.08)	29.96 <sup>e</sup> (-0.26)	46.21 <sup>e</sup> (0.03)	44.37 (-0.64)	29.81 (0.08)	0.15	0.13	2.85
1,4 <sup>A</sup> -(M) <sub>2</sub>	70.23 <sup>e</sup> (0.07)	39.43 (-0.10)	37.88 <sup>e</sup> (-0.01)	72.94 <sup>e</sup> (-0.42)	37.88 <sup>e</sup> (-0.01)	35.07 (-0.14)	29.52 <sup>e</sup> (-0.32)	46.10 <sup>e</sup> (-0.08)	39.43 (-0.10)	35.07 (-0.14)	0.06	0.22	2.88
2 <sup>E</sup> ,4 <sup>E</sup> -(M) <sub>2</sub>	33.96 <sup>e</sup> (-0.24)	73.17 <sup>e</sup> (-0.43)	42.59 (0.34)	73.17 <sup>e</sup> (-0.43)	33.96 <sup>e</sup> (-0.24)	31.19 (0.05)	26.80 (-0.11)	31.19 (0.05)	33.06 (-2.39)	24.84 <sup>e</sup> (0.35)	0.25	0.16	—
2 <sup>A</sup> ,4 <sup>E</sup> -(M) <sub>2</sub>	34.31 (0.11)	76.13 (2.53)	42.38 (0.13)	69.58 (1.46)	34.58 (0.00)	31.07 (-0.07)	26.33 (-0.20)	36.42 (-0.20)	30.25 <sup>f</sup> (0.28)	30.40 <sup>f</sup> (0.43)	0.30	0.22	—
2 <sup>A</sup> ,4 <sup>A</sup> -(M) <sub>2</sub>	35.37 <sup>e</sup> (0.79)	75.31 <sup>e</sup> (7.19)	41.01 (-1.24)	75.31 <sup>e</sup> (7.19)	35.37 <sup>e</sup> (0.79)	36.92 <sup>e</sup> (0.30)	26.33 (0.18)	36.92 <sup>e</sup> (0.30)	24.96 (0.47)	35.81 (0.36)	1.03	0.25	—
2,6-(M) <sub>2</sub> <sup>d</sup>	34.53 (-0.05)	74.57 <sup>e</sup> (-0.20)	33.99 (-0.21)	30.06 <sup>e</sup> (0.09)	34.53 (-0.05)	74.57 <sup>e</sup> (-0.20)	33.99 (-0.21)	30.06 <sup>e</sup> (0.09)	24.48 <sup>e</sup> (-0.01)	35.1 <sup>g</sup> (-0.4)	0.06	0.16	—

<sup>a</sup> The chemical shifts are in  $\delta$ -scale (ppm units, relative to  $(\text{CH}_3)_4\text{Si}$ ). The deviations  $\Delta$  are calculated as  $\Delta = \delta_{\text{exp}} - \delta_{\text{calc}}$ , where the  $\delta_{\text{exp}}$  are the experimental chemical shifts and  $\delta_{\text{calc}}$  are those calculated on the basis of direct additivity rule. The deviations are given in parenthesis. The adamantane carbon atoms are numbered according to the Scheme 1 and 2. <sup>b</sup> (M) stands for  $(\text{CH}_3)_3\text{SiO}$  group. Superscripts *E* and *A* denote equatorial and axial positions of the substituents, resp. <sup>c</sup> The indices (s) and (t) refer to (M) groups on secondary and tertiary carbon atoms, resp. <sup>d</sup> The position of 2-(M) groups is taken as *syn* to C-4 carbon atom. <sup>e</sup> The line assigned without any recourse to additivity rule. <sup>f</sup> The assignment uncertain, it can be reversed for the two lines. <sup>g</sup> Inaccurate position due to a computer failure.

substituents are unlikely (1,3- 1,4<sup>E</sup>- and 2,6-isomers) agree well (Table II) with the experimental shifts assigned without any use of the additivity rule. With the regards to the number of such lines and to the number of the independent substituent effects, the agreement proves the correctness of the assignments of the lines in the spectra of the monoderivatives (especially the signs and the magnitude of  $\gamma$  and  $\delta$  *syn* and *anti* effects) and proves that good additivity holds for the effects of the trimethylsiloxy groups if they do not interact sterically. The only exception being C-5 and C-7 carbon atoms of the 1,3-derivative in which two  $\gamma$  effects operate.

In the derivatives in which nonbonding interactions between the substituents occur, the deviations from additivity are considerable for the substituted carbon atoms, the other skeleton carbon shifts being much less affected. The second largest deviations are found for the carbon atoms subject to two  $\gamma$  interactions. (In haloadamantanes considerable deviations were also noted<sup>31</sup> only for such carbon atoms though the substituents were on the bridgehead carbon atoms). It should be noted that the deviations are largest (and of opposite signs) for the substituted carbon atoms of 1,2- and 2<sup>A</sup>,4<sup>A</sup>-isomers in which the crowding is most acute and in which also the extreme silicon chemical shifts were observed.

These findings demonstrate the utility of the additivity rules even for crowded adamantane derivatives and show that while the substituent's position on secondary or tertiary carbon atoms can be determined from either <sup>29</sup>Si or <sup>13</sup>C chemical shifts of the trimethylsiloxy group, the relative position of the two substituents can be determined from the adamantane skeleton carbon chemical shifts with the aid of the additivity rule. Usually one significant carbon shift can be found for distinguishing a pair of isomers (*e.g.* the 2,4-stereoisomers are best differentiated from  $\delta$ (C-9) values). In this way the structure of positional or configurational isomer of various adamantane derivatives can be determined after their conversion into trimethylsiloxy derivatives. The structural interpretation of their <sup>13</sup>C-NMR spectra is much simpler than that of <sup>1</sup>H-NMR spectra which require the use of shift reagents<sup>7-9</sup>.

As it is apparent from Table III all the absolute values of the substituent chemical shifts of the trimethylsiloxy group bonded to tertiary carbon atoms are larger than the corresponding substituent shifts of the group bonded to secondary carbon atoms (by about 15%). Inspection of the literature results<sup>25,26</sup> reveals that this is a general rule for adamantane derivatives with the exception of  $\beta$  effects of magnetically anisotropic substituents (CN, COOH).

A comparison with the pertinent substituent chemical shifts of the trimethylsiloxy group in cyclohexane (which are for the axial substituent:  $\alpha = 40.15$ ,  $\beta = 7.05$ ,  $\gamma_{\text{syn}} = -6.2$  and for the equatorial substituent;  $\alpha = 44.45$ ,  $\beta = 10.0$ ,  $\gamma_{\text{anti}} = -1.3$  and  $\delta_{\text{anti}} = -0.95$  ppm) according to the data of ref.<sup>33,34</sup> which are very close to the corresponding values of hydroxy group in cyclohexane<sup>35,36</sup> shows that the

rigidity (and perhaps strain) of the adamantane skeleton affects the more the substituent chemical shift, the closer the carbon atom is to the substituent. While the  $\delta_{\text{anti}}$  and  $\gamma_{\text{anti}}$  are practically the same in cyclohexyl and 2-adamantyl derivatives, the conformationally dependent  $\alpha$  effects in cyclohexane far exceed that in the 2-adamantyl derivative.

As already mentioned, the  $^{13}\text{C}$ -NMR spectra of trimethylsiloxyadamantanes are very similar to those of hydroxyadamantanes; this fact is well reflected in the similar magnitude and in the same sign of the corresponding substituent chemical shifts of hydroxy and trimethylsiloxy groups compared in Table III. Such similarity of substituent shifts (already noted in steroids<sup>40</sup>) can be easily rationalized in the case of  $\alpha$  and  $\beta$  substituents the effects of which are generally considered to be due essentially to inductive influences. Gamma substituent shifts, however, are usually regarded as being caused by steric interactions. Approximately the same  $\gamma_{\text{syn}}$  effects of hydroxy and trimethylsiloxy groups which differ so much in their steric requirements are hardly in accord with such an interpretation. At the same time, it is difficult to understand the opposite signs of  $\gamma_{\text{anti}}$  substituent chemical shifts of the substituents on secondary and tertiary carbon atoms. (In the recent work of Maciel and coworkers<sup>25</sup> similarly of  $\gamma_{\text{syn}}$  effects as well as the difference between  $\gamma_{\text{anti}}$  effects in 1- and 2-substituted adamantanes were noted for a number of other substituents but no comment was offered.) The positive  $\gamma_{\text{anti}}$  effects in 1-substituted adamantanes<sup>31,37</sup> form an exception<sup>32</sup> to the rule of Eliel and coworkers<sup>37</sup>. Since there cannot be any substantial nonbonded interaction between the substituent group and  $\gamma_{\text{anti}}$  carbon atom or the hydrogen atom bonded to it and since  $\gamma_{\text{anti}}$  effects correlate with inductive  $\sigma^*$  constant in a selected series of 1-substituted adamantanes<sup>26</sup>,

TABLE III  
 $^{13}\text{C}$  Substituent Chemical Shifts in Substituted Adamantanes<sup>a</sup>

Substituent <sup>b</sup>	$\alpha$	$\beta$	$\gamma_{\text{syn}}$	$\gamma_{\text{anti}}$	$\delta_{\text{syn}}$	$\delta_{\text{anti}}$	$\epsilon$
(CH <sub>3</sub> ) <sub>3</sub> SiO (t)	42.67	8.49	—	2.73	—	-1.31	—
(s)	37.08	7.09	-6.55	-1.07	-0.58	-0.96	+0.10
OH <sup>c</sup> (t)	39.05	7.83	—	2.43	—	-1.43	—
(s)	36.52	6.36	-6.73	-1.16	-0.71 <sup>d</sup>	-1.16 <sup>d</sup>	-0.07

<sup>a</sup> Substituent chemical shifts (SCS) calculated as the difference between the observed shifts of the corresponding carbons in the substituted and unsubstituted adamantanes. A positive value indicates a relative paramagnetic shift due to the substituent. <sup>b</sup> Indices (t) and (s) indicate position of the substituent on tertiary (C-1) and secondary (C-2) adamantane carbon atom resp. <sup>c</sup> Values taken from ref. <sup>25</sup>. <sup>d</sup> The assignment of ref. <sup>25</sup> inverted according to ref. <sup>28</sup>.

the origin of the different signs of  $\gamma_{\text{anti}}$  effects in 1- and 2-adamantyl derivatives is most likely in a different propagation of the inductive effect through C(t) – C(s) – C(t) and C(s) – C(t) – C(s) chains. In accord with such an interpretation is the observation of Pehk and Lippmaa<sup>35</sup> that in the case of the  $\gamma$ -interactions with the same substituent (*i.e.* C(s) – C(s) – C(s) chain) the  $\gamma$ -effects on carbon atoms are both only about 1.6 times smaller than in the case of 1-substituted compound (C(p) – C(s) – C(s) chain).

The  $\alpha$  carbon shift in 1-trimethylsiloxyadamantane fits the correlation<sup>26</sup> between the chemical shifts of the quarternary carbon atoms in 1-adamantyl and tert-butyl derivatives ( $\delta(C_{\text{quart}}) = 71.91$  in  $(\text{CH}_3)_3\text{SiOC}(\text{CH}_3)_3$ ). The correlation being apparently not affected by the size of the substituent and possible interactions with the  $\beta$  methylene group.

From the point of view of  $\beta$  substituent effects, Pehk, Lippmaa and coworkers<sup>26</sup> had to distinguish two types of substituents: those which contain no more than one atom heavier than hydrogen (these substituents shift the  $\beta$  carbon more than 5 ppm to a low field) and those substituent in which 1,4-interaction plays a significant role (and hence the lowfield shifts are less than 5 ppm). According to its structure, the trimethylsiloxy group should not belong to the former class of the substituents but the low-field shift of the  $\alpha$  carbon (7.8 ppm) places it there. The solution of this apparent dilemma is: the effect of oxygen atom of the trimethylsiloxy group is not compensated by the steric high-field shift since the necessary non-bonded interaction would not be of the usual 1,4- type but instead a smaller 1,5-interaction of adamantane methylene carbon with the methyl carbon of the substituent.

Similarly as recently found for other 2-adamantyl derivatives<sup>25,27</sup> we could differentiate  $\delta_{\text{syn}}$  and  $\delta_{\text{anti}}$  carbon atoms, but the observed diamagnetic shift agrees with the other findings of Pehk, Lippmaa and coworkers<sup>26</sup>. This small difference between *syn* and *anti*  $\delta$  carbon shifts clearly demonstrates the importance of the geometry factors (regarded<sup>26</sup> to be less likely source of the diamagnetic  $\delta$ -effects than the alternating charges) but it is not clear whether it is due to a small nonbonded interaction of the substituent with the carbon in question (as suggested by Duddeck<sup>27</sup>) or is it caused by small and different geometry changes induced in the two cyclohexane rings by the substituent which is axial ( $\delta_{\text{syn}}$ ) in one of the rings and equatorial ( $\delta_{\text{anti}}$ ) in the other. The difference between the  $\delta$  effects of hydroxy and trimethylsiloxy groups is not large enough to be conclusive in this respect.

Not negligible  $\epsilon$  substituent effects have been reported<sup>25,27</sup> for several substituents. Though these effects are smaller than the  $\delta$  effects they are in several cases also negative. This observation makes the interpretation of the  $\delta$  effect in the terms of alternating charges<sup>26,35</sup> questionable.

*Structural Considerations, Steric Effects*

Nonbonding interactions in a molecule lead to NMR observable effects if they change conformer population(s) or molecular geometry at the observed nucleus (or on the interconnecting chain), or if they alter the electron distribution around the nucleus in question. It is, however, only the last mentioned mechanism which gives rise to what is really meant by the term steric effect in NMR spectroscopy though it cannot be always separated from the other effects of nonbonding interactions.

The most popular mechanism of the steric effects in  $^{13}\text{C}$ -NMR spectroscopy which was suggested<sup>30</sup> for the 1-4 gauche interaction involves interaction of the terminal hydrogen (1-6) atoms which propagates to the bonded carbon atoms by a polarization of the C-H bonds. A similar interaction of the terminal methyl groups of the trimethylsiloxy groups could cause the silicon steric shifts by a polarization of the Si-C bonds. But since in the studied compounds methyl carbon shifts appear not to be related to the silicon steric shifts and vary only little with crowding, this mechanism must be disregarded. This mechanisms would be also incapable of accounting for the deviations of the adamantane skeleton  $^{13}\text{C}$  shifts from the additivity as observed in the crowded bis(trimethylsiloxy)adamantanes and dihydroxyadamantanes<sup>17</sup>.

At present we are not in a position to separate from the observed total effect the contribution of changed conformer populations. Changes in adamantane skeleton geometry must, however, be reflected in violations of additivity rule for skeleton carbon chemical shifts. Similar argument has been used in other studies to assess the geometry changes, most notably Pehk, Lippmaa and coworkers<sup>26</sup> took the already mentioned agreement of the calculated and experimental shifts for indicating absence of any large steric interactions and strain in adamantane (though it is estimated<sup>38,39</sup> to be destabilized by 8.8 kcal/mol relative to strain free fragments). In the studied bis(trimethylsiloxy)adamantanes the mean squared deviations of skeleton carbon shifts are rather small. Therefore one is led to the conclusion that if the second trimethylsiloxy group leads to changed molecular geometry, the change almost certainly does not involve all the skeleton carbon atoms. According to the deviations given in Table II any geometry change can involve only the substituted carbon atoms in the crowded molecules.

Since the largest deviations in carbon chemical shifts are accompanied by the largest diamagnetic steric shifts of silicon and these two effects seem to bear a clear relationship to the extent of molecular crowding as apparent from molecular models, the altered geometry at the substituted adamantane carbon atom must contribute to the observed silicon steric effects.

It is more likely, however, that an interaction of the nonbonding electrons of oxygen atoms propagates to the shielding of both silicon and substituted carbon nuclei. Such a mechanism was suggested for the interpretation of the steric effects



in *ortho* bis(trimethylsilyloxy)benzene<sup>3</sup>. Supporting evidence for this last mechanism was found in the spectra of dihydroxyadamantanes<sup>17</sup> in which similar deviations from additivity occur.

## REFERENCES

1. Schraml J., Chvalovský V., Mägi M., Lippmaa E., Galas R., Dunoguès J., Bourgeois P.: *J. Organometal. Chem.* **120**, 41 (1976).
2. Lippmaa E., Mägi M., Chvalovský V., Schraml J.: *This Journal* **42**, 318 (1977).
3. Schraml J., Chvalovský V., Jancke H., Engelhardt G.: *Org. Magn. Resonance* **9**, 237 (1977).
4. Engelhardt G., Schraml J.: *Org. Magn. Resonance* **9**, 239 (1977).
5. Schraml J., Pola J., Jancke H., Engelhardt G., Černý M., Chvalovský V.: *This Journal* **41**, 360 (1977).
6. Schraml J., Pola J., Chvalovský V., Marsmann H. C., Bláha K.: *This Journal* **42**, 1165 (1977).
7. Mohyla I., Ksandr Z., Hájek M., Vodička L.: *This Journal* **39**, 2935 (1974).
8. Hájek M., Vodička L., Hlavatý J.: *Org. Magn. Resonance* **7**, 529 (1975).
9. Vodička L., Hájek M., Ksandr Z., Hlavatý J.: *This Journal* **40**, 293 (1975).
10. Janků J., Burkhard J., Vodička L.: *Czech. No* 163618.
11. Landa S., Kriebel S., Knobloch E.: *Chem. Listy* **48**, 61 (1954).
12. Stetter H., Schwarz H., Hirschhorn A.: *Ber. Deut. Chem. Ges.* **92**, 1629 (1959).
13. Schleyer P. R., Nicholas R. D.: *J. Amer. Chem. Soc.* **83**, 182 (1961).
14. Cuddy B. D., Grant D., McKervey M. A.: *J. Chem. Soc. (C)* **3173** (1971).
15. Geluk H. W., Schlatmann J. L. M. A.: *Tetrahedron* **24**, 5369 (1968).
16. Vodička L., Hlavatý J.: *This Journal*, in press.
17. Schraml J., Jancke H., Engelhardt G., Vodička L., Hlavatý J.: *This Journal*, in press.
18. Janků J., Landa S.: *This Journal* **35**, 375 (1970).
19. Snatzke G., Marquarding D.: *Ber. Deut. Chem. Ges.* **100**, 1710 (1967).
20. Mironov V. F., Fedotov N. S.: *Zh. Obshch. Khim.* **42**, 166 (1972).
21. Pola J., Papoušková Z., Chvalovský V.: *This Journal* **41**, 239 (1976).
22. Mägi M., Lippmaa E., Chvalovský V., Schraml J.: Unpublished results.
23. Charton M.: *J. Org. Chem.* **29**, 12222 (1964).
24. Alper H., Keung E. C. H., Partis R. A.: *J. Org. Chem.* **36**, 1352 (1971).
25. Maciel G. E., Dorn H. C., Greene R. L., Kleschick W. A., Peterson jr M. R., Wahl jr G. H.: *Org. Magn. Resonance* **6**, 178 (1974).
26. Pehk T., Lippmaa E., Sevestyanova V. V., Krayuschkin M. M., Tarasova A. I.: *Org. Magn. Resonance* **3**, 783 (1971).
27. Duddeck H.: *Org. Magn. Resonance* **7**, 151 (1975).
28. Duddeck H., Dietrich W.: *Tetrahedron Lett.* **33**, 2925 (1975).
29. Berger S., Zeller K. P.: *J. Chem. Soc., Chem. Commun.* **649** (1976).
30. Grant D. M., Paul E. G.: *J. Amer. Chem. Soc.* **86**, 2984 (1964).
31. Perkins R. R., Pincok R. E.: *Org. Magn. Resonance* **8**, 165 (1976).
32. Duddeck H., Wolff P.: *Org. Magn. Resonance* **8**, 593 (1976).
33. Schneider H. J., Hornung R.: *Justus Liebigs Ann. Chem.* **1864** (1974).
34. Breitmaier E., Voelter W.: <sup>13</sup>C-NMR *Spectroscopy*, p. 122. Verlag Chemie, Weinheim 1974.
35. Pehk T., Lippmaa E.: *Org. Magn. Resonance* **3**, 679 (1971).
36. Pehk T., Kooskora H., Lippmaa E.: *Org. Magn. Resonance* **8**, 5 (1976).

37. Eliel E. L., Bailey W. F., Kopp L. D., Willer R. L., Grant D. M., Bertrand R., Christensen K. A., Dalling D. K., Duch M. W., Wenkert E., Schell F. M., Cochran D. W.: *J. Amer. Chem. Soc.* 97, 322 (1975).
38. Grant D. M., Cheeney B. V.: *J. Amer. Chem. Soc.* 89, 5315 (1967).
39. Liebman J. F., Greenberg A.: *Chem. Rev.* 76, 313 (1976).
40. Engelhardt G., Zeigan D., Schönecker B.: *J. Prakt. Chem.*, in press.

Translated by the author (J. S.).