

## <sup>13</sup>C Chemical Shifts of Di- and Triamantanes: A Similar Effect of a Methyl Substituent on Adamantanes

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**Abstract:** *Di- and triamantanes are interesting models to probe substituent effects on adamantanes. The rigid structure of the carbon skeleton does not allow the same relief of angular strain. Also, steric effects are also reflected by changes in carbon-carbon bond lengths and concomitant shielding or deshielding. The introduction of a methyl group as substituent in secondary and tertiary positions of the adamantane system provides a convenient rationalization for the main variations in <sup>13</sup>C chemical shifts observed for non-substituted di- and triamantane relative to adamantane.*

**Resumo:** *Di- e triamantanos são modelos interessantes para se provar o efeito de substituintes em adamantanos. A estrutura rígida do esqueleto de carbono não permite o mesmo alívio de tensão angular e efeitos estéricos também são refletidos por mudanças nos comprimentos de ligação carbono-carbono e concomitante blindagem ou desblindagem. A introdução de um grupo metila como substituinte na posição secundária e terciária do sistema adamantano permite racionalizar as principais variações nos deslocamentos químicos de <sup>13</sup>C observados para o di- e triamantano não substituídos com relação ao adamantano.*

### Introduction

Substituent effects are widely used to investigate factors affecting chemical shifts. Among the most important ones are steric effects, which are used to determine molecular structure. Duddeck et al. showed that adamantanes, di- and triamantanes are excellent models for the study of these effects.<sup>1</sup> Our recent works on mono- and disubstituted adamantanes<sup>2,3</sup> have revealed that steric effects can contribute to substituent

chemical shifts for both neighboring and distant nuclei and may be transmitted through space or through bonds. They also show that substituent effects on chemical shifts could be traced to make changes in molecular geometry and charge distribution. This data can be used to evaluate the shape and volume of the groups that are involved in steric interactions.<sup>2,3</sup>

Di- and triamantanes (Figure 1) are particularly well suited to investigate how far different substituents affect NMR chemical shifts and probe substituent effects observed

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for substituted adamantanes. The more rigid carbon skeleton does not allow the same angular relief of strain, and steric effects are also reflected by changes in carbon-carbon bond lengths and concomitant shielding or deshielding. Additionally, these systems are very interesting because they correspond to the adamantane with methyl substituents in

positions 4, 6 and 10 (diamantane) and also in position 3 (triamantane). This fact allows the use of our rationalizations for substituted adamantanes in order to investigate the reasons why the largest differences in  $^{13}\text{C}$  chemical shifts of non-substituted di- and triamantane related to adamantane occur mainly in the ring junctions (Table 1).

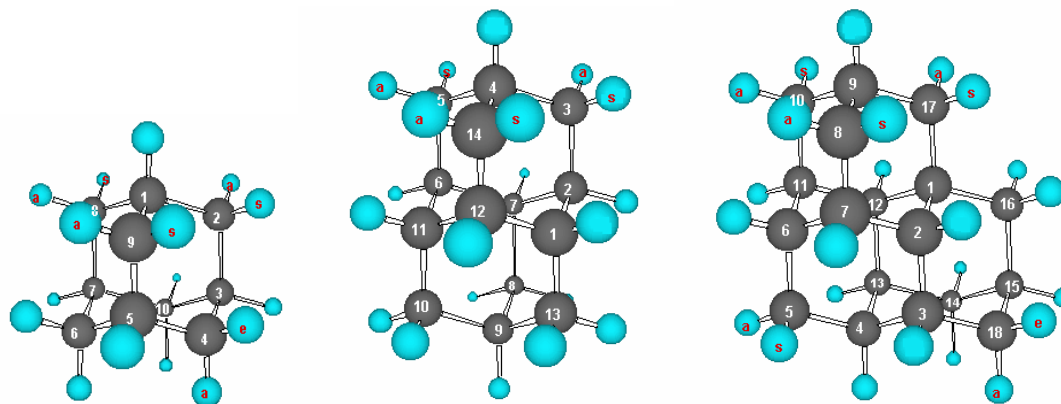


Figure 1. Adamantane, di- and triamantane, respectively

### Experimental

All experimental carbon-13 chemical shifts were obtained from reference 1. The geometries of the compounds studied were optimized in the Gaussian 98 program<sup>4</sup> by using DFT method and B3LYP/6-31G(d,p) basis set.

### Results and Discussion

Some of the effects caused by the introduction of a methyl group in the secondary position of adamantane (2-methyladamantane) are as follows: the stretching of  $\text{C}_\alpha\text{-C}_\beta$  bonds and the inverse bond polarization effect<sup>5</sup> of the C-H bond geminal to the substituent (Table 2), which leads to a deshielding process in the chemical shifts of the carbon-13 involved in these bonds (Table 1). These effects can be also noticed in di- and triamantanes, when we

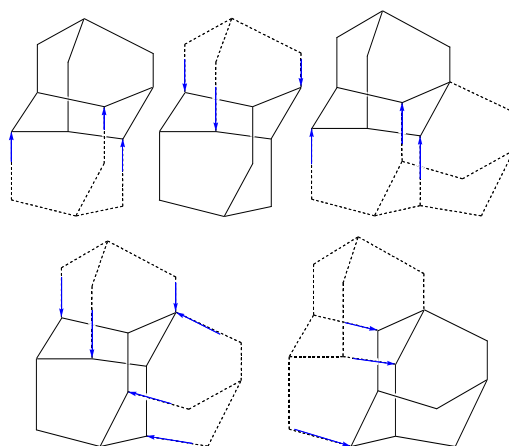
consider that they are adamantanes with “methyl” substituents (Figure 2).

A similar effect of the methyl group introduction in secondary position of adamantane occurs for di- and triamantane: all

the  $C_{\alpha}$ - $C_{\beta}$  and C-H bonds of the ring junctions (where the “substituents” are introduced) are stretched in di- and triamantanes compared to the adamantane system.

**Table 1.**  $^{13}\text{C}$  chemical shifts (ppm) of adamantane, diamantane, triamantane and methyladamantanes<sup>1</sup>

	Adamantane	Diamantane	Triamantane	1-methyl adamantane	2-methyl adamantane
<b>C<sub>1</sub></b>	28.5	37.7	33.6	29.7	34.0
<b>C<sub>2</sub></b>	37.8	37.7	46.9	44.6	39.1
<b>C<sub>3</sub></b>	28.5	38.4	38.1	28.9	34.0
<b>C<sub>4</sub></b>	37.8	26.0	35.3	38.9	31.4
<b>C<sub>5</sub></b>	28.5	38.4	38.6	28.9	28.6
<b>C<sub>6</sub></b>	37.8	37.7	35.3	36.9	38.7
<b>C<sub>7</sub></b>	28.5	37.7	38.1	28.9	28.3
<b>C<sub>8</sub></b>	37.8	38.4	38.1	44.6	39.6
<b>C<sub>9</sub></b>	37.8	26.0	27.8	44.6	31.4
<b>C<sub>10</sub></b>	37.8	38.4	38.1	36.9	39.6
<b>C<sub>11</sub></b>	---	37.7	38.1	---	---
<b>C<sub>12</sub></b>	---	37.7	46.9	---	---
<b>C<sub>13</sub></b>	---	38.4	38.1	---	---
<b>C<sub>14</sub></b>	---	38.4	38.1	---	---
<b>C<sub>15</sub></b>	---	---	27.8	---	---
<b>C<sub>16</sub></b>	---	---	45.3	---	---
<b>C<sub>17</sub></b>	---	---	45.3	---	---
<b>C<sub>18</sub></b>	---	---	38.1	---	---



**Figure 2.** Introduction of “methyl groups” (arrows in blue) in secondary positions of adamantane (full lines) in di- and triamantanes

**Table 2.** Bond lengths (Å) of adamantane, diamantane, triamantane and methyladamantanes calculated by the Gaussian 98 program

	Adamantane	Diamantane	Triamantane	1-methyl adamantane	2-methyl adamantane
<b>C<sub>1</sub>-C<sub>2</sub></b>	1.544	1.550	1.559	1.548	1.552
<b>C<sub>1</sub>-C<sub>8</sub></b>	1.544	---	---	1.549	1.544
<b>C<sub>1</sub>-C<sub>9</sub></b>	1.544	---	---	1.548	1.544
<b>C<sub>1</sub>-C<sub>12</sub></b>	---	1.551	1.560	---	---
<b>C<sub>1</sub>-C<sub>13</sub></b>	---	1.541	---	---	---
<b>C<sub>1</sub>-C<sub>16</sub></b>	---	---	1.541	---	---
<b>C<sub>1</sub>-C<sub>17</sub></b>	---	---	1.541	---	---
<b>C<sub>2</sub>-C<sub>3</sub></b>	1.544	1.540	1.547	1.542	1.552
<b>C<sub>2</sub>-C<sub>7</sub></b>	---	1.551	1.548	---	---
<b>C<sub>3</sub>-C<sub>4</sub></b>	1.544	1.541	1.548	1.542	1.545
<b>C<sub>3</sub>-C<sub>10</sub></b>	1.544	---	---	1.543	1.544
<b>C<sub>3</sub>-C<sub>18</sub></b>	---	---	1.539	---	---
<b>C<sub>4</sub>-C<sub>5</sub></b>	1.544	1.541	1.538	1.543	1.544
<b>C<sub>4</sub>-C<sub>14</sub></b>	---	1.541	---	---	---
<b>C<sub>5</sub>-C<sub>6</sub></b>	1.544	1.540	1.538	1.543	1.543
<b>C<sub>5</sub>-C<sub>9</sub></b>	1.544	---	---	1.543	1.544
<b>C<sub>6</sub>-C<sub>7</sub></b>	1.544	1.551	1.548	1.543	1.543
<b>C<sub>6</sub>-C<sub>11</sub></b>	---	1.550	1.548	---	---
<b>C<sub>7</sub>-C<sub>8</sub></b>	1.544	1.540	1.540	1.543	1.544
<b>C<sub>7</sub>-C<sub>10</sub></b>	1.544	---	---	1.543	1.543
<b>C<sub>8</sub>-C<sub>9</sub></b>	---	1.541	1.541	---	---
<b>C<sub>9</sub>-C<sub>10</sub></b>	---	1.541	1.541	---	---
<b>C<sub>9</sub>-C<sub>13</sub></b>	---	1.541	---	---	---
<b>C<sub>9</sub>-C<sub>17</sub></b>	---	---	1.540	---	---
<b>C<sub>10</sub>-C<sub>11</sub></b>	---	1.540	1.540	---	---
<b>C<sub>11</sub>-C<sub>12</sub></b>	---	1.551	1.547	---	---
<b>C<sub>12</sub>-C<sub>13</sub></b>	---	---	1.548	---	---
<b>C<sub>12</sub>-C<sub>14</sub></b>	---	1.540	---	---	---
<b>C<sub>13</sub>-C<sub>14</sub></b>	---	---	1.539	---	---
<b>C<sub>14</sub>-C<sub>15</sub></b>	---	---	1.541	---	---
<b>C<sub>15</sub>-C<sub>16</sub></b>	---	---	1.541	---	---
<b>C<sub>15</sub>-C<sub>18</sub></b>	---	---	1.541	---	---
<b>C<sub>1</sub>-H<sub>1</sub></b>	1.098	1.099	---	---	1.098
<b>C<sub>2</sub>-H<sub>2(a)</sub></b>	1.098	1.099	1.101	1.099	1.101
<b>C<sub>2</sub>-H<sub>2s</sub></b>	1.098	---	---	1.099	---
<b>C<sub>3</sub>-H<sub>3(a)</sub></b>	1.098	1.098	1.100	1.098	1.098
<b>C<sub>3</sub>-H<sub>3s</sub></b>	---	1.098	---	---	---
<b>C<sub>4</sub>-H<sub>4(a)</sub></b>	1.098	1.097	1.099	1.098	1.098
<b>C<sub>4</sub>-H<sub>4e</sub></b>	1.098	---	---	1.098	1.097
<b>C<sub>5</sub>-H<sub>5(a)</sub></b>	1.098	1.098	1.098	1.098	1.098
<b>C<sub>5</sub>-H<sub>5s</sub></b>	---	1.098	1.098	---	---

**Continuation of Table 2.** Bond lengths (Å) of adamantane, diamantane, triamantane and methyladamantanes calculated by the Gaussian 98 program

	Adamantane	Diamantane	Triamantane	1-methyl adamantane	2-methyl adamantane
<b>C<sub>6</sub>-H<sub>6a</sub></b>	1.098	1.099	1.099	1.098	1.098
<b>C<sub>6</sub>-H<sub>6s(e)</sub></b>	1.098	---	---	1.098	1.098
<b>C<sub>7</sub>-H<sub>7</sub></b>	1.098	1.099	1.100	1.098	1.098
<b>C<sub>8</sub>-H<sub>8a</sub></b>	1.098	1.098	1.098	1.099	1.098
<b>C<sub>8</sub>-H<sub>8s(e)</sub></b>	1.098	1.098	1.098	1.099	1.098
<b>C<sub>9</sub>-H<sub>9(a)</sub></b>	1.098	1.097	1.098	1.099	1.098
<b>C<sub>9</sub>-H<sub>9s</sub></b>	1.098	---	---	1.099	1.097
<b>C<sub>10</sub>-H<sub>10a</sub></b>	1.098	1.098	1.098	1.098	1.098
<b>C<sub>10</sub>-H<sub>10s(e)</sub></b>	1.098	1.098	1.098	1.098	1.098
<b>C<sub>11</sub>-H<sub>11</sub></b>	---	1.099	1.100	---	---
<b>C<sub>12</sub>-H<sub>12</sub></b>	---	1.099	1.101	---	---
<b>C<sub>13</sub>-H<sub>13(a)</sub></b>	---	1.098	1.100	---	---
<b>C<sub>13</sub>-H<sub>13s</sub></b>	---	1.098	---	---	---
<b>C<sub>14</sub>-H<sub>14a</sub></b>	---	1.098	1.098	---	---
<b>C<sub>14</sub>-H<sub>14s(e)</sub></b>	---	1.098	1.098	---	---
<b>C<sub>15</sub>-H<sub>15</sub></b>	---	---	1.098	---	---
<b>C<sub>16</sub>-H<sub>16a</sub></b>	---	---	1.099	---	---
<b>C<sub>16</sub>-H<sub>16s</sub></b>	---	---	1.099	---	---
<b>C<sub>17</sub>-H<sub>17a</sub></b>	---	---	1.099	---	---
<b>C<sub>17</sub>-H<sub>17s</sub></b>	---	---	1.099	---	---
<b>C<sub>18</sub>-H<sub>18a</sub></b>	---	---	1.098	---	---
<b>C<sub>18</sub>-H<sub>18e</sub></b>	---	---	1.098	---	---

Thus, there is charge redistribution (Table 3) and these effects are associated with the deshielding observed for carbons of the ring junctions of the tertiary carbons of non substituted adamantanes. This reflects not only the inverse bond polarization effect<sup>5</sup> but also C-C bond stretching.

For triamantane, it is also observed the effect of the methyl substituent introduction on

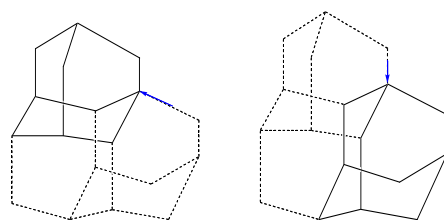
a tertiary position of adamantane (Figure 3). When a methyl group is introduced in this position (1-methyl adamantane), not only C<sub>α</sub>-C<sub>β</sub> bonds are stretched, but also an inverse bond polarization effect is observed for C<sub>β</sub>-H<sub>β</sub> bonds (Table 2). As consequence, the β carbons are deshielded (Table 1).

**Table 3.** Charge densities of adamantane, diamantane, triamantane and methyladamantanes calculated by the Gaussian 98 program

	Adamantane	Diamantane	Triamantane	1-methyl adamantane	2-methyl adamantane
<b>C<sub>1</sub></b>	-0.064	-0.058	0.037	0.038	-0.059
<b>C<sub>2</sub></b>	-0.167	-0.057	-0.054	-0.160	-0.041
<b>C<sub>3</sub></b>	-0.064	-0.174	-0.063	-0.070	-0.060
<b>C<sub>4</sub></b>	-0.167	-0.062	-0.056	-0.167	-0.172
<b>C<sub>5</sub></b>	-0.065	-0.173	-0.179	-0.069	-0.064
<b>C<sub>6</sub></b>	-0.167	-0.058	-0.056	-0.167	-0.168
<b>C<sub>7</sub></b>	-0.064	-0.058	-0.063	-0.069	-0.063
<b>C<sub>8</sub></b>	-0.168	-0.173	-0.173	-0.160	-0.173
<b>C<sub>9</sub></b>	-0.167	-0.062	-0.067	-0.160	-0.172
<b>C<sub>10</sub></b>	-0.168	-0.174	-0.173	-0.167	-0.173
<b>C<sub>11</sub></b>	---	-0.057	-0.063	---	---
<b>C<sub>12</sub></b>	---	-0.058	-0.054	---	---
<b>C<sub>13</sub></b>	---	-0.173	-0.063	---	---
<b>C<sub>14</sub></b>	---	-0.173	-0.173	---	---
<b>C<sub>15</sub></b>	---	---	-0.067	---	---
<b>C<sub>16</sub></b>	---	---	-0.170	---	---
<b>C<sub>17</sub></b>	---	---	-0.169	---	---
<b>C<sub>18</sub></b>	---	---	-0.173	---	---
<b>H<sub>1</sub></b>	0.072	0.067	---	---	0.068
<b>H<sub>2(a)</sub></b>	0.081	0.067	0.062	0.079	0.073
<b>H<sub>2s</sub></b>	0.081	---	---	0.079	---
<b>H<sub>3(a)</sub></b>	0.072	0.081	0.066	0.072	0.068
<b>H<sub>3s</sub></b>	---	0.081	---	---	---
<b>H<sub>4(a)</sub></b>	0.081	0.071	0.066	0.081	0.082
<b>H<sub>4e</sub></b>	0.081	---	---	0.081	0.084
<b>H<sub>5(a)</sub></b>	0.072	0.081	0.080	0.072	0.071
<b>H<sub>5s</sub></b>	---	0.081	0.080	---	---
<b>H<sub>6(a)</sub></b>	0.081	0.067	0.066	0.081	0.081
<b>H<sub>6s</sub></b>	0.081	---	---	0.082	0.081
<b>H<sub>7</sub></b>	0.072	0.067	0.066	0.072	0.072
<b>H<sub>8a</sub></b>	0.081	0.081	0.080	0.079	0.081
<b>H<sub>8s</sub></b>	0.081	0.081	0.081	0.079	0.081
<b>H<sub>9(a)</sub></b>	0.081	0.071	0.070	0.079	0.082
<b>H<sub>9s</sub></b>	0.081	---	---	0.079	0.084
<b>H<sub>10a</sub></b>	0.081	0.081	0.080	0.081	0.081
<b>H<sub>10s</sub></b>	0.081	0.081	0.081	0.081	0.081
<b>H<sub>11</sub></b>	---	0.067	0.066	---	---
<b>H<sub>12</sub></b>	---	0.067	0.062	---	---
<b>H<sub>13a</sub></b>	---	0.081	0.066	---	---
<b>H<sub>13s</sub></b>	---	0.081	---	---	---
<b>H<sub>14a</sub></b>	---	0.081	0.080	---	---

**Continuation of Table 3.** Charge densities of adamantane, diamantane, triamantane and methyladamantanes calculated by the Gaussian 98 program

	Adamantane	Diamantane	Triamantane	1-methyl adamantane	2-methyl adamantane
<b>H<sub>14e</sub></b>	---	0.081	0.081	---	---
<b>H<sub>15</sub></b>	---	---	0.070	---	---
<b>H<sub>16a</sub></b>	---	---	0.078	---	---
<b>H<sub>16s</sub></b>	---	---	0.078	---	---
<b>H<sub>17a</sub></b>	---	---	0.078	---	---
<b>H<sub>17s</sub></b>	---	---	0.078	---	---
<b>H<sub>18a</sub></b>	---	---	0.080	---	---
<b>H<sub>18e</sub></b>	---	---	0.081	---	---

**Figure 3.** Introduction of “methyl groups” (arrows in blue) in tertiary positions of adamantane (full lines) in triamantanes

The same analysis can be applied to triamantanes, which justifies the deshielding of  $C_2$ ,  $C_{12}$ ,  $C_{16}$  and  $C_{17}$ . But for  $C_2$  and  $C_{12}$  there is a superposition of the effect of a methyl group introduction in secondary and tertiary positions of adamantane. Thus, the biggest inverse bond polarizations are observed for  $C_2$ - $H_2$  and  $C_{12}$ - $H_{12}$  bonds in triamantane, and the biggest bond stretching (around 0.015 Å) is observed for  $C_1$ - $C_2$  and  $C_1$ - $C_{12}$  ( $C_\alpha$ - $C_\beta$  bonds) because of a “methyl group” introduced in each carbon involved in these bonds. As consequence,  $C_2$

and  $C_{12}$  are the most deshielded carbons of the triamantane structure.

For  $C_4$  and  $C_6$ , there is a competition between stretching in the ring junction bonds and the short bond lengths of  $C_4$ - $C_5$  and  $C_5$ - $C_6$  (0.006 Å shorter than the corresponding C-C bonds in adamantane). These carbons are shielded in relation to the secondary carbons of adamantane and deshielded in relation to the tertiary ones.

For non substituted di- and triamantanes, C-C bond lengths are the main responsables for variations on  $^{13}\text{C}$  chemical shifts of

adamantanes: where the C-C bond length is stretched, the carbon nuclei is deshielded and where the C-C bond length is shortened, the carbon nuclei is shielded. This is what seems to generally occur, except for secondary carbons from di- and triamantanes, where there is a shortness of the C-C bond length, but the carbon nuclei is deshielded in relation to the correspondent carbons in the adamantane system. However, this deshielding is very slight, shorter than 1 ppm

### Conclusions

The effect of methyl substituents in the adamantane system allowed us to rationalize the variations of  $^{13}\text{C}$  chemical shifts observed for di- and triamantane in relation to adamantane.

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