

## Hydrogen Chemical Shifts as Probes for Steric Effects in Haloadamantanes

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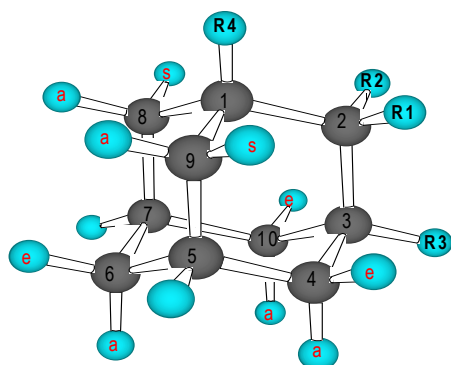
**Abstract:** *The most important single experimental parameter in NMR spectroscopy is the chemical shift, and hydrogen chemical shifts have been compiled and interpreted for many years. However, chemical shifts described in stereochemistry studies used to be almost exclusively associated with  $^{13}\text{C}$  nuclei. Our recent work has shown that hydrogen chemical shifts can be used in order to identify steric effects too. The present work represents an extension of our studies on adamantanes substituted at positions 1 and 2. We have compared the effect of bromine with Me, Et, *i*-Pr and *t*-Bu groups. In the present work, chlorine (which is smaller) and iodine (which is larger) are compared to bromine as substituents. In view of the problems inherent in making calculations on heavy atoms such as halogens, we have used experimental chemical shifts to verify the extent of steric substituent effects on hydrogen at different positions. For neighboring atoms, the order  $I > Br > Cl$  is observed for substituents at both positions; thus the degree of deshielding of hydrogens responds to the size of the substituent. In the case of the substituent on a tertiary carbon, an inversion is observed for the deshielding of hydrogens on the  $\gamma$ -carbon. This effect may be explained by the fact that bromine stretches the  $C_2-C_3$  bond, increasing the chemical shift of  $C_3$ , which decreases the chemical shift of  $H_3$ .*

The most important single experimental parameter in NMR spectroscopy is the chemical shift, and hydrogen chemical shifts have been compiled and interpreted for many years.<sup>1</sup> However, chemical shifts described in stereochemistry studies used to be almost exclusively associated with  $^{13}\text{C}$  nuclei. Our recent work<sup>2</sup> has shown that hydrogen chemical shifts can be also used in order to identify steric effects.

The present work represents an extension of our studies<sup>3</sup> on adamantanes (Figure 1) substituted at positions 1 and 2. In reference 4

we compared the effect of bromine with Me, Et, *i*-Pr and *t*-Bu groups. In the present work, chlorine (which is smaller) and iodine (which is larger) are compared to bromine as substituents. Theoretical calculations were run using the Gaussian 98 program<sup>5</sup> with GIAO method and B3LYP/6-31G(d,p) basis set.

In view of the problems inherent in making calculations using heavy atoms such as halogens, we have used experimental chemical shifts<sup>6,7</sup> to verify the extent of steric substituent effects on hydrogen at different positions (Table 1).



	<b>R1</b>	<b>R4</b>
<b>1</b>	H	Cl
<b>2</b>	H	Br
<b>3</b>	H	I
<b>4</b>	Cl	H
<b>5</b>	Br	H
<b>6</b>	I	H

**Figure 1.** Substituted Adamantanes

**Table 1.** Observed differences between substituted adamantane and adamantane  $^1\text{H}$  chemical shifts.

	1	2	3	4	5	6
H <sub>1</sub>	---	---	---	0.20	0.28	0.29
H <sub>2a</sub>	0.39	0.62	0.88	2.65	2.92	3.25
H <sub>2s</sub>	0.39	0.62	0.88	---	---	---
H <sub>3</sub>	0.27	0.23	0.10	0.20	0.28	0.29
H <sub>4a</sub>	-0.08	-0.02	0.11	-0.18	-0.13	-0.04
H <sub>4e</sub>	-0.08	-0.02	0.11	0.52	0.59	0.63
H <sub>5</sub>	0.27	0.23	0.10	-0.01	0.01	0.03
H <sub>6a</sub>	-0.08	-0.02	0.11	0.01	-0.01	0.04
H <sub>6e</sub>	-0.08	-0.02	0.11	0.01	-0.01	0.04
H <sub>7</sub>	0.27	0.23	0.10	-0.01	0.01	0.03
H <sub>8a</sub>	0.39	0.62	0.88	0.20	0.11	0.20
H <sub>8s</sub>	0.39	0.62	0.88	0.05	0.22	0.20
H <sub>9a</sub>	0.39	0.62	0.88	-0.18	-0.13	-0.04
H <sub>9s</sub>	0.39	0.62	0.88	0.52	0.59	0.63
H <sub>10a</sub>	-0.08	-0.02	0.11	0.20	0.11	0.20
H <sub>10e</sub>	-0.08	-0.02	0.11	0.05	0.22	0.20

For neighboring atoms, the order  $\text{I} > \text{Br} > \text{Cl}$  is observed for substituents at both positions, thus the degree of deshielding of hydrogens responds to the size of the substituent.<sup>3</sup> In the case of the substituent on a tertiary carbon (1-3), an inversion is observed for deshielding of hydrogens on the  $\gamma$ -carbon. This effect may be explained by the fact that bromine stretches the  $\text{C}_2\text{-C}_3$  bond by 0.001 angstrom relative to chlorine,

increasing the chemical shift of  $\text{C}_3$  and thus decreasing the chemical shift of  $\text{H}_3$ .<sup>3</sup>

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