

Filtration and evaporation of the solvent gave 90 mg of **15** as a colorless crystallization product: sublimation at 80–90 °C (1 torr); mp (sealed tube) 134–135 °C; IR 3630 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.00 (s, 3 H), 1.06 (s, 3 H), 2.53 (s, 1 H), 4.33 (sept, 1 H).

**9,9-Dimethylbicyclo[3.3.1]nonan-3-endo-ol (16)**. The hydrogenation of **14** was achieved by stirring the reaction mixture under hydrogen atmosphere for 14 h. Usual workup and recrystallization from aqueous methanol afforded colorless needles: mp 41 °C dec; IR 3600 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 0.88 (s, 3 H), 1.00 (s, 3 H), 4.08 (m, 1 H).

**9,9-Dimethylbicyclo[3.3.1]nonan-3-one (12)**. Hydrogenation of 165 mg of **11** in the same conditions gave 160 mg of saturated ketone **12** as oily product which crystallized slowly on cooling: sublimation at 80–90 °C (1 torr); mp 73–75 °C; IR 1715 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.16 (s, 6 H).

**9,9-Dimethylbicyclo[3.3.1]nonan-3-one Ethylene Acetal (17)**. A mixture of 100 mg of **12**, 10 mL of benzene, 10 mg of *p*-TSA, and 0.1 mL of 1,2-ethanediol was refluxed for 6 h. The usual workup gave 140 mg of crude product as a mixture of **17** along with the starting material. Separation by flash chromatography yielded 77 mg of **17** as a colorless oil: IR 1095 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.05 (s, 6 H), 3.56 (m, 4 H). **12** (21 mg) was obtained as colorless crystals.

**9,9-Dimethylbicyclo[3.3.1]nonane-3,7-dione (5)**. A solution of the Michael adduct **3** (2.2 g) and NaOH (2.0 g) in methanol (50 mL) and water (50 mL) was refluxed overnight under argon,

cooled, and acidified with 10% aqueous HCl. The aqueous solution was extracted with ethyl acetate to yield 1.25 g of white solid product. Recrystallization from ether gave **5** as colorless crystals: mp 127–128 °C; IR 1710 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.40 (s, 6 H); <sup>13</sup>C NMR δ 26.2 (q), 32.7 (s), 41.2 (d), 45.1 (t), 208.7 (s). Anal. Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>: C, 73.30; H, 8.95. Found: C, 73.05; H, 8.80.

**Sodium Borohydride Reduction of the Diketone 5. The Hemiacetal 6**. Sodium borohydride (18 mg, 0.45 mmol) was added to a stirred solution of the diketone **5** (320 mg, 1.78 mmol) in 95% ethanol (5 mL). After 20 min, water (1 mL) was added and the mixture refluxed gently for 15 min. More water was added, and the solution extracted with ether, which was then dried and evaporated. Flash chromatography of the crude product gave 200 mg of the hemiacetal **6** which crystallized from pentane-ether: mp (sealed tube) 192–193 °C; IR 3600, 1190 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.10 (s, 6 H), 4.23 (m, 1 H), 4.35 (s, 1 H). Anal. Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>: C, 72.49; H, 9.96. Found: C, 72.12; H, 9.64.

**Registry No.** 1, 1073-14-9; 2, 1830-54-2; 3 (isomer 1), 94519-31-0; 3 (isomer 2), 94519-32-1; 3 (7-ketal), 94519-43-4; 4, 37741-10-9; 5, 37741-08-5; 6, 94519-33-2; 7, 94519-34-3; 8, 94519-35-4; 9, 94519-36-5; 9 (thiocarbonate), 94519-44-5; 10, 94519-37-6; 10 (ketal), 94519-45-6; 11, 94519-38-7; 12, 75984-11-1; 13, 94519-39-8; 14, 94519-40-1; 15, 75984-06-4; 16, 75984-16-6; 17, 94519-41-2; 18, 75984-22-4; 19, 94519-42-3; 1,2-ethanediol, 107-21-1; *p*-tolyl chlorothioformate, 937-63-3; diethyl chlorophosphate, 814-49-3.

## Substituent Effects on <sup>13</sup>C NMR Chemical Shifts and One-Bond <sup>13</sup>C–<sup>13</sup>C Coupling Constants in 1- and 4-Substituted Diamantanes

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One-bond <sup>13</sup>C–<sup>13</sup>C NMR coupling constants in a series of 1- and 4-substituted diamantanes were measured at natural abundance by using the INADEQUATE pulse sequence. The substituent effect on <sup>13</sup>C chemical shifts (SCS) and <sup>13</sup>C–<sup>13</sup>C coupling constants (SCC) was analyzed in terms of the electronegativity and steric effects of the substituents and in terms of the number and type of the gauche interaction. The trends observed in the C<sub>α</sub>–C<sub>β</sub>, C<sub>β</sub>–C<sub>γanti</sub>, and C<sub>β</sub>–C<sub>γsyn</sub> coupling constants are in accord with results obtained on 1- and 2-substituted adamantanes.

Recent advances in instrumentation and the availability of high-field NMR spectrometers have greatly increased the scope and utility of <sup>13</sup>C–<sup>13</sup>C NMR coupling constants in structural studies. While recent theoretical studies<sup>1,2</sup> have reproduced certain qualitative trends in experimental values, they are still far from giving quantitative agreements. Thus, there has been considerable effort to obtain more extensive experimental values of *J*<sub>CC</sub><sup>3–6</sup> and to find

empirical correlations with other molecular properties which are dependent on the same electronic characteristic of the molecules.

The basic problem in observing the <sup>13</sup>C–<sup>13</sup>C coupling constants in the NMR spectra of compounds with natural abundance <sup>13</sup>C is that of identifying the appropriate weak satellite signals on the sides of strong <sup>13</sup>C lines. The INADEQUATE pulse sequence technique developed by Freeman et al.<sup>7</sup> enables one to investigate one-bond and long-range carbon-carbon couplings by suppressing the strong signals from molecules with isolated <sup>13</sup>C nucleus.

Although substituent effects on *J*<sub>CC</sub> values have been studied<sup>2,8,9</sup> to some extent, mostly with <sup>13</sup>C-labeled compounds, studies of stereochemical effects on *J*<sub>CC</sub> values

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Table I.  $^{13}\text{C}$  NMR Chemical Shifts in 1-Substituted Diamantanes (1)<sup>a</sup>

X	$\delta_{\text{C}_1}$	$\delta_{\text{C}_2}$	$\delta_{\text{C}_3}$	$\delta_{\text{C}_4}$	$\delta_{\text{C}_5}$	$\delta_{\text{C}_6}$	$\delta_{\text{C}_7}$	$\delta_{\text{C}_8}$	$\delta_{\text{C}_9}$	$\delta_{\text{C}_{13}}$	other
H	37.7	37.7	38.4	26.0	38.4	37.7	37.7	38.4	26.0	38.4	
CH <sub>3</sub>	34.0	42.1	33.2	26.2	39.0	37.6	38.6	38.5	28.1	46.9	26.5
OCH <sub>3</sub>	73.7	39.5	32.0	25.0	37.8	36.8	39.5	37.2	29.7	39.2	46.3
F	94.4	41.7	32.4	24.8	37.5	36.3	40.6	36.9	30.6	43.0	
Cl	76.5	44.9	33.3	25.0	38.1	36.2	40.8	37.1	30.7	49.3	
Br	78.7	46.0	34.6	25.1	38.5	36.4	41.3	37.1	31.3	51.5	
I	70.4	48.0	37.3	25.4	39.2	36.7	41.0	37.4	31.6	55.6	

<sup>a</sup>The chemical shifts measured in CDCl<sub>3</sub> at room temperature are in ppm with respect to external Me<sub>4</sub>Si and are accurate to  $\pm 0.1$  ppm.

Table II.  $^{13}\text{C}$  NMR Chemical Shifts in 4-Substituted Diamantanes (2)<sup>a</sup>

X	$\delta_{\text{C}_4}$	$\delta_{\text{C}_3}$	$\delta_{\text{C}_2}$	$\delta_{\text{C}_1}$	$\delta_{\text{C}_8}$	$\delta_{\text{C}_9}$	other
H	26.0	38.4	37.7	37.7	38.4	26.0	
CH <sub>3</sub>	27.7	45.4	38.3	36.9	38.0	25.9	30.3
OCH <sub>3</sub>	70.5	40.8	39.1	36.8	36.3	25.2	47.5
F	92.4	42.9	40.3	36.8	36.2	25.4	
Cl	67.2	47.8	40.2	35.5	36.6	25.0	
Br	65.2	49.5	41.3	35.6	36.9	25.0	
I	49.4	52.8	41.9	35.6	37.1	25.0	

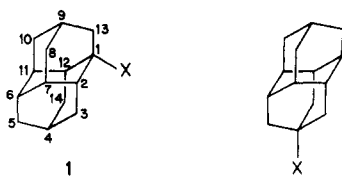
<sup>a</sup>The chemical shifts measured in CDCl<sub>3</sub> at room temperature are in ppm with respect to external Me<sub>4</sub>Si and are accurate to  $\pm 0.1$  ppm.

Table III. One-Bond  $^{13}\text{C}$ - $^{13}\text{C}$  Coupling Constants in 1-Substituted Diamantanes (1)<sup>a</sup>

X	$J_{\alpha,\beta}$		$J_{\beta,\gamma_{\text{anti}}}$		$J_{\beta,\gamma_{\text{syn}}}$		$J_{\gamma,\delta}$			$J_{\delta,\epsilon}$		other
	$J_{1,2}$	$J_{1,13}$	$J_{2,7}$	$J_{9,13}$	$J_{2,3}$	$J_{3,4}$	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{4,5}$	$J_{5,6}$	
H		<i>b</i>		31.6	<i>b</i>	31.6		<i>b</i>	31.6	31.6	<i>b</i>	
CH <sub>3</sub>	30.7	31.9	30.6	31.7	32.2	31.7	<i>b</i>	<i>b</i>	31.7	31.6	<i>b</i>	37.2
OCH <sub>3</sub>	35.1	34.6	<i>b</i>	31.6	32.5	31.5	30.7	32.1	31.6	31.6	<i>b</i>	
F	35.2	34.7	29.4	31.3	32.1	31.7	30.6	32.2	31.3	31.7	<i>b</i>	
Cl	34.4	33.4	28.6	31.1	32.9	31.6	30.6	32.3	31.7	31.5	32.1	
Br	32.3	32.4	28.0	30.6	33.1	31.6	30.5	32.5	31.8	31.6	32.3	
I	30.7	31.7	27.6	30.0	33.3	31.7	30.8	32.1	31.8	31.6	32.1	

<sup>a</sup>All coupling constants are in Hz and within  $\pm 0.2$  Hz in CDCl<sub>3</sub> at room temperature. <sup>b</sup>Could not be measured accurately due to peak overlap.

have not yet been explored.<sup>3,4,10-12</sup> The development of the INADEQUATE pulse sequence by Freeman et al.<sup>7</sup> to measure  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants in natural-abundance  $^{13}\text{C}$  NMR spectra seems to open up a new avenue to study substituent and stereochemical effects on  $J_{\text{CC}}$  in a wide variety of compounds. The most suitable model compounds for such investigations are those having rigid frameworks with well-defined geometries, such as derivatives of diamondoid hydrocarbons. We recently reported<sup>13</sup> our study on substituent effect on  $^{13}\text{C}$ - $^{13}\text{C}$  NMR coupling constants (SCC) in 1- and 2-substituted adamantanes. Two- and three-bond  $^{13}\text{C}$ - $^{13}\text{C}$  NMR coupling constants in 2-substituted adamantanes have also been reported.<sup>14</sup> In continuation of our study on SCC in diamondoid molecules we now report the results of our studies on 1- and 4-substituted diamantanes (1 and 2, respectively).



X = H, CH<sub>3</sub>, OCH<sub>3</sub>, F, Cl, Br, I

Table IV. One-Bond  $^{13}\text{C}$ - $^{13}\text{C}$  Coupling Constants in 4-Substituted Diamantanes (2)<sup>a</sup>

X	$J_{3,4}$	$J_{2,3}$	$J_{1,2}$	$J_{1,13}$	$J_{8,9}$	other
H	31.6	<i>b</i>		<i>b</i>	31.6	
CH <sub>3</sub>	32.2	32.2	30.5	32.2	31.7	37.2
OCH <sub>3</sub>	35.9	31.3	30.5	<i>b</i>	31.8	
F	35.7	32.0	30.6	32.2	31.7	
Cl	33.7	30.6	30.7	32.2	31.7	
Br	33.1	29.7	30.6	32.1	31.6	
I	32.4	29.4	30.6	32.2	31.6	

<sup>a</sup>All coupling constants are in Hz and are within  $\pm 0.2$  Hz in CDCl<sub>3</sub> at room temperature. <sup>b</sup>Could not be measured due to peak overlap.

## Results and Discussion

The  $^{13}\text{C}$  chemical shifts ( $\delta_{\text{C}}$ ) and one-bond carbon-carbon coupling constants in 1-substituted diamantanes (1) and 4-substituted diamantanes (2) were measured along with those of the parent diamantane (1-H). The chemical shifts of some of the mono-substituted diamantanes have been reported earlier.<sup>15-17</sup> However, present study includes a more extended series of substituents and for comparison all the  $^{13}\text{C}$  NMR chemical shifts in the diamantane derivatives studied in this work are listed in Tables I and II. The assignment of the chemical shifts is in accord with those already reported<sup>16-18</sup> or based on proton multiplicities

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**Table V. Comparison of Substituent Effect on  $^{13}\text{C}$  Chemical Shifts (SCS) in Bridgehead-Substituted Adamantanes and Diamantanes<sup>a</sup>**

	X	1-Ad-X <sup>b</sup>	1-X	2-X	
$\alpha$ -SCS	CH <sub>3</sub>	+1.4	-3.7	+1.7	
	OCH <sub>3</sub>	+43.4	+36.0	+43.5	
	F	+63.8	+56.7	+66.4	
	Cl	+39.8	+38.8	+41.2	
	Br	+38.0	+41.0	+39.2	
	I	+22.1	+32.7	+23.4	
	X	1-Ad-X <sup>b</sup>	C <sub>2</sub>	C <sub>13</sub>	2-X
$\beta$ -SCS	CH <sub>3</sub>	+7.0	+4.4	+8.5	+7.0
	OCH <sub>3</sub>	+3.4	+1.8	+0.8	+2.4
	F	+5.0	+4.0	+4.6	+4.5
	Cl	+9.7	+7.2	+10.9	+9.4
	Br	+11.5	+8.3	+13.1	+11.1
	I	+14.5	+10.3	+17.2	+14.4

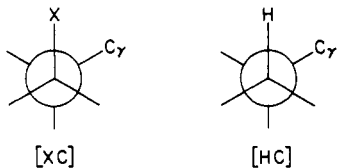
<sup>a</sup>All SCS values are in ppm and are within  $\pm 0.1$  ppm.

<sup>b</sup>Reference 13.

observed in APT (attached proton test)<sup>18</sup> spectra. The  $^{13}\text{C}$ - $^{13}\text{C}$  NMR coupling constants listed in Tables III and IV were obtained from natural abundance spectra using the INADEQUATE<sup>7</sup> pulse sequence.

**$^{13}\text{C}$  NMR Chemical Shifts.** Substituent effects on  $^{13}\text{C}$  chemical shifts (SCS) in substituted adamantanes, diamantanes, and triamantanes have been studied earlier by Duddeck et al.<sup>15</sup> Since the present study includes additional substituents, the  $\alpha$ -SCS and  $\beta$ -SCS values in 1- and 4-substituted diamantanes are compared with those in 1-substituted adamantanes<sup>13,15</sup> in Table V.

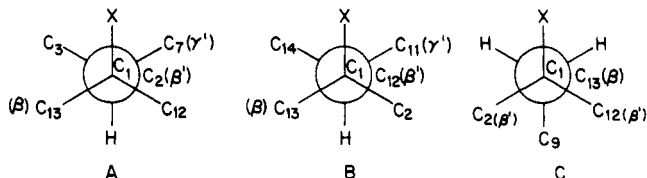
Analysis of the  $\alpha$ -SCS values in Table V indicates that the  $\alpha$ -substituent effect is the same in 1-adamantyl and 4-diamantyl derivatives. However, the  $\alpha$ -SCS values are quite different in the 1-diamantyl derivatives. It has been pointed out<sup>15,19</sup> that for bridgehead-substituted compounds the large differences in  $\alpha$ -SCS are mainly caused by the varying number of the gauche interactions (XC)<sup>20</sup> between



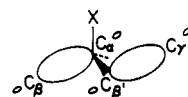
the substituent X and the  $\gamma$  carbon atoms. The gauche interaction XC replaces the interaction HC so that the net contribution from the X-C interaction is [XC-HC].<sup>19</sup> In 4-substituted diamantanes and 1-substituted adamantanes no [XC-HC] interaction is present, whereas in 1-substituted diamantanes two  $\gamma$ -gauche interactions exist. From these  $\alpha$ -SCS values [XC-HC] contributions can be estimated ( $\pm 1$  ppm): [CC-HC]  $\sim -3$  ppm; [OC-HC]  $\sim -4$  ppm; [FC-HC]  $\sim -4$  ppm; [ClC-HC]  $\sim -1$  ppm; [BrC-HC]  $\sim +1$  ppm; [IC-HC]  $\sim +5$  ppm. From these estimates a qualitative sequence of the XC interactions can be deduced: IC > BrC > HC > ClC > CC > OC  $\approx$  FC. Earlier, on the basis of a limited number of  $\gamma$ -gauche interaction estimates it was stated<sup>15</sup> that the XC gauche interactions are governed neither by the electronegativity of X nor by steric repulsion. However, in the present study we have estimated the XC gauche interactions for all the halogen substituents and an oxygen substituent. From this qualitative sequence it can be concluded that the XC gauche interactions are governed both by electronegativity

of X and by steric repulsion. The "electronegativity" contribution seems to be a shielding effect and the "steric" contribution is a deshielding one. Among the halogen series the electronegativity effect dominates for F and Cl while the steric effect dominates for Br and I. However, it seems to be premature at this point to evaluate the individual contributions.

$\beta$ -SCS values (cf. Table V) in 1-adamantyl and 4-diamantyl derivatives are comparable while the two  $\beta$ -SCS values ( $\Delta\delta_{\text{C}_{13}}$  and  $\Delta\delta_{\text{C}_2}$ ) in 1-diamantyl derivatives are quite different. The  $\beta$ -SCS values for C<sub>13</sub> is generally higher than the  $\beta$ -SCS values for C<sub>2</sub> or C<sub>12</sub>. This has been earlier<sup>15</sup> attributed to the presence of two C <sub>$\gamma$</sub>  atoms (C<sub>7</sub> and C<sub>11</sub> in structures A and B, respectively) antiperiplanar to C<sub>13</sub>



while one exists for C<sub>2</sub> (C<sub>14</sub> in structure B) and C<sub>12</sub> (C<sub>3</sub> in structure A). This has been explained by a delocalization of the charge polarization at the  $\beta$ -carbon atom via an interaction of the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  with the parallel C <sub>$\beta$</sub> -C <sub>$\gamma$</sub>  bond orbital.<sup>15</sup>



**$^{13}\text{C}$ - $^{13}\text{C}$  NMR Coupling Constants.** The C<sub>3</sub>-C<sub>4</sub> coupling constant ( $J_{3,4}$ ) in diamantane (1-H) is the same as that in adamantane itself (31.6 Hz). However, the C<sub>2</sub>-C<sub>3</sub> coupling constant ( $J_{2,3}$ ) could not be measured in diamantane. The C<sub>2</sub> and C<sub>3</sub> resonances are too close to each other and thus represent a strongly coupled AB spin system. Reasonable signal-to-noise ratio could not be achieved to identify the outer weak peaks of this AB quartet. Our earlier study<sup>13</sup> on 1- and 2-substituted adamantanes has shown that methyl groups have only a limited effect on the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  coupling constants ( $J_{\alpha,\beta}$ ) and no effect on the C <sub>$\beta$</sub> -C <sub>$\gamma$</sub>  and C <sub>$\gamma$</sub> -C <sub>$\delta$</sub>  coupling constants ( $J_{\beta,\gamma}$  and  $J_{\gamma,\delta}$ ). Thus in the following discussion the coupling constants in methyladamantane would be taken as the reference values.

(a) **4-Substituted Diamantanes.** The C<sub>4</sub>-C<sub>3</sub> (C <sub>$\alpha$</sub> -C <sub>$\beta$</sub> ) coupling constant ( $J_{3,4}$ ) in 4-substituted diamantanes (2-X) decreases in the order 2-F  $\approx$  2-CH<sub>3</sub>O > 2-Cl > 2-Br > 2-I  $\approx$  2-CH<sub>3</sub> > 2-H. The substituent effect observed on the  $J_{3,4}$  values is qualitatively correlated with the inductive electron-withdrawing ability (or electronegativity) of the substituent. For example, in 4-fluorodiamantane (2-F), with the most electron-withdrawing substituent the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  coupling constant is 35.7 Hz (3.5 Hz larger than that in 4-methyldiamantane, 2-CH<sub>3</sub>, or 4.1 Hz larger than that in diamantane) whereas in 4-iododiamantane (2-I) the value is 32.4 (only 0.8 Hz larger than that in diamantane). This qualitative relationship between  $J_{3,4}$  and the electronegativity of the substituents in 2-X is in line with the earlier observation in 1-substituted adamantanes<sup>13</sup> and in *tert*-butyl derivatives.<sup>13,21</sup>

The C <sub>$\beta$</sub> -C <sub>$\gamma$</sub>  (C<sub>3</sub>-C<sub>2</sub>) coupling constants ( $J_{3,2}$ ) in 4-substituted diamantanes follow the trend 2-F > 2-OCH<sub>3</sub> > 2-Cl > 2-Br > 2-I. This trend is again in line with the earlier observation in substituted adamantanes. Although

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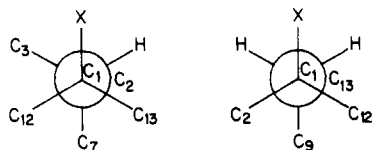
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this trend is the same as that observed in  $C_\alpha-C_\beta$  ( $C_4-C_3$ ) coupling constants, it must be noted that the substituent effects are in the opposite direction. In other words, while  $J_{C_\alpha-C_\beta}$  increases on substitution,  $J_{C_\beta-C_\gamma}$  decreases.

The substituents have very little effect on the coupling constants between the remote carbons.

**(b) 1-Substituted Diamantanes.** The  $C_\alpha-C_\beta$  ( $C_1-C_2$  and  $C_1-C_{13}$ ) and  $C_\beta-C_{\gamma_{anti}}$  ( $C_2-C_7$  and  $C_{13}-C_9$ ) coupling constants in 1-substituted diamantanes (1-X) follow the same qualitative trend as observed in 4-substituted diamantanes and 1-substituted adamantanes.<sup>13</sup> However the coupling constant values in 1-substituted diamantanes are of further interest in that there are two  $C_\alpha-C_\beta$  ( $C_1-C_2$  and  $C_1-C_{13}$ ) and two  $C_\beta-C_{\gamma_{anti}}$  bonds ( $C_2-C_7$  and  $C_{13}-C_9$ ) in this case.

A closer examination of the coupling constant values in Table III reveals that the magnitude of the substituent effect on  $J_{1,2}$  is larger compared to that on  $J_{1,13}$ . The  $J_{1,2}$  value increases by 4.5 Hz on going from 1-iododiamantane to 1-fluorodiamantane, while  $J_{1,13}$  increases only by 3.0 Hz. Similarly, the magnitude of the substituent effect on  $J_{2,7}$  is more compared to that on  $J_{13,9}$ . The  $J_{2,7}$  value changes by 1.8 Hz between 1-iododiamantane and 1-fluorodiamantane, while  $J_{13,9}$  changes only by 1.3 Hz. If one examines the Newman projection formulae through the  $C_\alpha-C_\beta$  bonds, it is evident that in one case ( $C_\beta:C_2$ ) there is a  $\bar{C}-X$  gauche interaction while in the other ( $C_\beta:C_{13}$ ) there is none.



As discussed earlier the trends observed in the substituent effect on the  $\alpha$ -carbon chemical shifts ( $\alpha$ -SCS) and the  $\beta$ -carbon chemical shifts ( $\beta$ -SCS) can be interpreted in terms of the number of gauche interactions.<sup>15</sup> It is quite possible that similar gauche interactions between the substituent and  $C_3$  may be responsible for the observed differences in the  $\alpha$ -SCS and  $\beta$ -SCS values in 1-substituted diamantanes.

The  $C_2-C_3$  coupling constant in 1-X is also of interest in that the  $C_2-C_3$  bond is gauche to the  $C_1-X$  bond. It can be noted that the  $C_2-C_3$  ( $C_\beta-C_{\gamma_{syn}}$ ) coupling constant increases as the bulkiness of the heteroatom containing the lone pair electrons increases (i.e.,  $I > Br > Cl > O > F$ ). It has been shown earlier that no substituent effect is observed with bulky alkyl substituents.<sup>13</sup> This gauche effect by the lone-pair electrons on  $C_\beta-C_{\gamma_{syn}}$  coupling constant is in line with our earlier observation in 2-substituted adamantanes and also with that observed by Barna and Robinson<sup>10</sup> in the derivatives of piperidine and cyclohexanone.

As in the case of 4-substituted diamantanes no significant substituent effect was observed on coupling constants between the remote carbons.

### Conclusions

We have determined the substituent effect on one-bond  $^{13}C-^{13}C$  NMR coupling constants in a series of 1- and 4-substituted diamantanes, remarkably rigid cage compounds, particularly suited to evaluate steric interactions. The substituent effect on the  $^{13}C$  NMR chemical shifts ( $\alpha$ -SCS and  $\beta$ -SCS) and on  $^{13}C-^{13}C$  coupling constants ( $C_\alpha-C_\beta$  SCC,  $C_\beta-C_{\gamma_{anti}}$  SCC, and  $C_\beta-C_{\gamma_{syn}}$  SCC) were evaluated in terms of the electronegativity and steric effects of the substituent and in terms of the number and type of gauche interactions. The present results are compli-

mentary to our earlier reported study<sup>13</sup> on substituted adamantanes and extend our understanding of the effect of substituents on  $^{13}C-^{13}C$  NMR coupling constants and the qualitative trends discussed in terms of electronegativity effects and gauche interactions. However, more detailed experimental and theoretical studies are needed before more quantitative evaluation of these substituent effects will be possible.

### Experimental Section

All diamantane derivatives were prepared from diamantane<sup>22</sup> through various literature routes. 1-Bromodiamantane, 1-Br [mp 221–222 °C (lit.<sup>23</sup> mp 222–224 °C)], was prepared from direct bromination of diamantane.<sup>23</sup> Other 1- and 4-substituted diamantanes were prepared from the corresponding diamantanols, 1-OH [mp 287–290 °C (lit.<sup>22</sup> mp 291–292 °C)] and 2-OH [mp 253–254 °C (lit.<sup>22</sup> mp 256–257 °C)], which were in turn prepared from diamantane itself.<sup>22</sup> 4-Bromodiamantane, 2-Br [mp 125–126 °C (lit.<sup>22</sup> mp 127–128 °C)], was prepared by the reaction of 4-diamantanol with 48% HBr.<sup>22</sup> Conversion of diamantanols to the corresponding fluorodiamantanes, 1-F [mp 223–224 °C (lit.<sup>17</sup> mp 223–224 °C)] and 2-F [mp 218–220 °C (lit.<sup>17</sup> mp 218–220 °C)], was achieved by using PPHF reagent.<sup>24</sup> Diamantanols could be converted to the corresponding iododiamantanes, 1-I [mp 160–163 °C. Anal. Found: C, 53.21; H, 6.34; I, 40.45. Calcd C, 53.5; H, 6.1; I, 40.4] and 2-I [mp 130–131 °C. Anal. Found: C, 53.41; H, 6.30; I, 40.41. Calcd C, 53.5; H, 6.1; I, 40.4%] using  $CH_3SiCl_3/NaI$ .<sup>25</sup> Reaction of diamantanols with  $SOCl_2/Py$  yielded the corresponding chlorodiamantanes, 1-Cl [mp 244–245 °C (lit.<sup>22</sup> mp 250–252 °C)] and 2-Cl [mp 73–74 °C (lit.<sup>22</sup> mp 75–76 °C)]. Diamantanols can be methylated to the corresponding methoxy diamantanes, 1-OCH<sub>3</sub> [mp 115–116 °C. Anal. Found: C, 82.64; H, 10.01; O, 7.3. Calcd C, 82.6; H, 10.1; O, 7.3] and 2-OCH<sub>3</sub> [mp 81–83 °C. Anal. Found: C, 82.45; H, 10.25; O, 7.35. Calcd C, 82.6; H, 10.1; O, 7.3], using  $CH_3I/NaH$ .<sup>15</sup> 1-Methyl and 4-methyldiamantanes, 1-CH<sub>3</sub> [mp 212–214 °C (lit.<sup>26</sup> mp 215–218 °C)] and 2-CH<sub>3</sub> [mp 96–97 °C (lit.<sup>26</sup> mp 98–99 °C)], were prepared by the reaction of  $CH_3MgBr$  with the corresponding bromodiamantanes.<sup>26</sup> All compounds used were purified (>99%) by recrystallization or by chromatography and gave satisfactory NMR spectra.

Proton noise decoupled  $^{13}C$  NMR, APT (attached proton test or spin-echo Fourier transform)  $^{13}C$  NMR, and  $^{13}C$  satellite spectra were recorded at 50 MHz on a Varian XL-200 superconducting NMR spectrometer equipped with a variable-temperature broad-band probe. All the spectra were recorded in  $CDCl_3$  at room temperature ( $\sim 20$  °C) unless otherwise stated.

The pulse sequence used for the  $^{13}C$  satellite spectra, based on Freeman et al.,<sup>7</sup> is  $90^\circ(x)-\tau-180^\circ(\pm y)-\tau-90^\circ(x)-\Delta-90^\circ(\phi)-Acq(\psi)$ , where  $\tau \approx (2n+1)/4J_{CC}$ ,  $\Delta$  is a very short delay ( $\sim 10$   $\mu s$ ) needed to reset the radiofrequency phase, and  $\phi$  and  $\psi$  are the phase of the last  $90^\circ$  "read" pulse and the receiver, respectively. Optimum setting of  $\tau$  for direct coupling is when  $n = 0$  and thus set at 7.0 ms (corresponding to a  $J_{CC}$  value of  $\sim 36$  Hz). The repetition rate of this sequence is  $\sim 10$  s, and reasonable signal to noise ratio was achieved in 6–8 h of acquisition.

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**Registry No.** 1 (X = H), 2292-79-7; 1 (X = CH<sub>3</sub>), 26460-76-4; 1 (X = OCH<sub>3</sub>), 95193-09-2; 1 (X = F), 77052-09-6; 1 (X = Cl), 32401-16-4; 1 (X = Br), 30545-17-6; 1 (X = I), 77062-71-6; 2 (X = CH<sub>3</sub>), 28375-86-2; 2 (X = OCH<sub>3</sub>), 95193-10-5; 2 (X = F), 77052-10-9; 2 (X = Cl), 32401-17-5; 2 (X = Br), 30545-30-3; 2 (X = I), 77052-11-0.

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