

### <sup>13</sup>C Nuclear Magnetic Resonance Spectra. Part 10.<sup>1</sup> Substituent Effects on the <sup>13</sup>C Chemical Shifts of Adamantanes, Diamantanes, and Triamantanes

By Helmut Duddeck,\* Ruhr-Universität Bochum, Abteilung für Chemie, Postfach 10 21 48, D-4630 Bochum 1, West Germany

Frederick Hollowood, Amna Karim, and M. Anthony McKervey, Department of Chemistry, University College, Cork, Ireland

The <sup>13</sup>C n.m.r. data of a variety of substituted adamantanes, diamantanes, and triamantanes are presented. The  $\alpha$ -substituted chemical shifts (SCS) can be described by gauche XC interactions, the magnitudes of which decrease in the sequence BrC > HC > OC  $\approx$  CC. Similarly, gauche interactions of the types HX and CX contribute to the  $\beta$ -SCS, but additionally the  $\beta$ -SCS are increased, if the  $\beta$ -carbon atoms possess antiperiplanar  $\gamma'$ -carbon atoms. Steric interaction of the substituent with gauche  $\gamma$ -carbon atoms seem to cause rather downfield rather than upfield shifts of the  $\gamma$ -signals. The hyperconjugative interaction of parallel C $\alpha$ -C $\beta$ - and C $\beta$ '-C $\alpha'$ -bond orbitals increase the  $\gamma_{anti}$ -SCS of the hydroxy and, to a smaller extent, the bromine substituent.

ALTHOUGH a lot of empirical material about substituent effects on <sup>13</sup>C chemical shifts (SCS) has been published during the recent years,<sup>2</sup> the mechanisms of SCS are not yet understood completely. The most suitable model compounds for such investigations are those having rigid frameworks with well defined geometries, such as adamantane derivatives. This study deals with SCS in adamantanes, diamantanes, and triamantanes, particularly the last, featuring a variety of different, though

related configurations of the substituents so that configurational influences on the SCS can be investigated.

*Assignments.*—The assignment of the <sup>13</sup>C n.m.r. spectra of all compounds in this study is based on off-resonance (SFORD) spectra. The spectra of some monosubstituted adamantanes,<sup>3-7</sup> of (3c and d)<sup>8</sup> and of diamantane (6a)<sup>9</sup> have been published before, but for comparison all the data given in Tables 1 and 2, except those for (3b),<sup>10</sup> were obtained by ourselves. The

TABLE 1  
<sup>13</sup>C Chemical shifts and SCS (in parentheses) of mono- and di-substituted adamantanes<sup>a</sup>

Compound	Carbon atom										Others
	1	2	3	4	5	6	7	8	9	10	
(1a)	28.5	37.8	28.5	37.8	28.5	37.8	28.5	37.8	37.8	37.8	
(1b)	29.7	44.6	28.9	38.9	28.9	36.9	28.9	44.6	44.6	36.9	31.3 (CH <sub>3</sub> )
(1c)	67.9	45.3	30.8	(-0.9)	30.8	36.1	30.8	45.3	(6.8)	(-0.9)	36.1
(1d)	66.5	49.4	32.6	(2.3)	32.6	35.7	32.6	49.4	(7.5)	(7.5)	35.7
(1e)	71.9	41.2	30.7	(4.1)	30.7	36.7	30.7	41.2	(11.6)	(11.6)	36.7
(1f)	51.6	41.5	29.4	(-1.1)	29.4	36.4	29.4	41.5	(3.4)	(3.4)	36.4
(2b)	34.0	39.1	34.0	(0.9)	31.4	28.6	38.7	28.3	(-1.4)	(-1.4)	39.6
(2c)	34.7	74.7	34.7	(5.5)	31.2	27.8	37.8	27.3	(1.8)	(-6.2)	31.2
(2d)	36.5	63.7	36.5	(-6.6)	31.7	27.7	38.0	27.0	(3.6)	(-6.6)	31.7
(2e)	31.5	83.3	31.5	(8.0)	31.5	27.6	37.7	27.6	(1.0)	(-6.1)	31.5
(2f)	32.1	53.5	32.1	(3.0)	32.0	27.4	37.7	27.3	(45.5)	(-6.3)	32.0
(3b) <sup>b</sup>	37.4	(15.7)	37.4	(3.6)	33.3	27.7	39.3	27.7	(-1.2)	(-6.3)	37.3
(3c)	39.3	73.8	39.3	(-5.8)	33.1	27.2	38.5	27.7	(-0.5)	(-5.8)	33.1
(3d)	42.2	82.3	42.2	(3.4)	33.3	27.7	39.3	27.7	(-0.5)	(-5.8)	33.3
(4a)	31.1	46.8	31.1	(-6.3)	33.1	27.2	38.5	27.7	(1.8)	(-6.3)	31.1
(4c)	35.8	75.6	35.8	(-6.3)	33.1	27.2	38.5	27.7	(1.8)	(-6.3)	31.1
(4d)	38.2	80.2	38.2	(-6.3)	33.1	27.2	38.5	27.7	(1.8)	(-6.3)	31.1
(5c)	68.9	52.2	33.4	(-4.3)	31.0	35.4	31.0	44.6	(3.7)	(-6.5)	33.4
(5d)	65.7	55.9	35.0	(2.1)	32.5	34.7	32.5	48.4	(7.7)	(7.7)	35.0
	(36.8)	(11.3)	(5.3)	(-2.1)	(3.6)	(-2.2)	(3.6)	(11.5)	(11.5)	(-2.1)	(-1.2)

<sup>a</sup> In p.p.m. relative to tetramethylsilane. Positive SCS correspond to downfield shifts. Chemical shift values marked by \* or † may be interchanged. <sup>b</sup> Data taken from ref. 10; the shift of C-2 is not reported.

TABLE 2  
<sup>13</sup>C Chemical shifts and SCS (in parentheses) of mono-substituted diamantanes <sup>a</sup>

Com- pound	Carbon atom														Others
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
(6a)	37.7	37.7	38.4	26.0	38.4	37.7	37.7	38.4	26.0	38.4	37.7	37.7	38.4	38.4	
(6b)	34.0	42.2	33.3	28.2	39.1	37.7	38.7	38.6	26.2	38.6	38.7	42.2	47.0	33.3	26.6
(6c)	(-3.7)	(4.5)	(-5.1)	(2.2)	(0.7)	(0.0)	(1.0)	(0.2)	(0.2)	(0.2)	(1.0)	(4.5)	(8.6)	(-5.1)	(CH <sub>3</sub> )
(6d)	70.8	43.4	32.6	25.3	38.0	36.8	40.0	37.6	30.5	37.6	40.0	43.4	46.4	32.6	
(7b)	(33.1)	(5.7)	(-5.8)	(-0.7)	(-0.4)	(-0.9)	(2.3)	(-0.8)	(4.5)	(-0.8)	(2.3)	(5.7)	(8.0)	(-5.8)	
(7c)	31.6	43.3	40.1	31.6	39.9	37.5	39.4	38.3	26.7	38.4	38.4	38.0	38.4	32.4	18.0
(7d)	(-6.1)	(5.6)	(1.7)	(5.6)	(1.5)	(-0.2)	(1.7)	(-0.1)	(0.7)	(0.7)	(0.7)	(0.3)	(0.0)	(-6.0)	(CH <sub>3</sub> )
(8b)	31.5	43.9	75.4	32.4	37.6	36.5	36.9	36.6	26.6	38.0	37.6	37.0	37.6	32.0	
(8c)	(-6.2)	(6.2)	(37.0)	(6.4)	(-0.8)	(-1.2)	(-0.8)	(-1.8)	(0.6)	(-0.4)	(-0.1)	(-0.7)	(-0.8)	(-6.4)	
(8d)	31.7	45.2	64.0	34.1	38.9	36.1	39.7	37.4	25.9	37.7	37.9	36.9	37.7	32.6	
(9)	(-6.0)	(7.5)	(25.6)	(8.1)	(0.5)	(-1.6)	(2.0)	(-1.0)	(-0.1)	(-0.7)	(0.2)	(-0.8)	(-0.7)	(-5.8)	
(9)	37.0	38.4	45.5	27.7	45.5	38.4	37.0	38.0	26.0	38.0	37.0	38.4	38.0	45.5	30.3
(9)	(-0.7)	(0.7)	(7.1)	(1.7)	(7.1)	(0.7)	(-0.7)	(-0.4)	(0.0)	(-0.4)	(-0.7)	(0.7)	(-0.4)	(7.1)	(CH <sub>3</sub> )
(9)	36.4	39.9	45.7	67.5	45.7	39.9	36.4	37.3	25.7	37.3	36.4	39.9	37.3	45.7	
(9)	(-1.3)	(2.2)	(7.3)	(41.5)	(7.3)	(2.2)	(-1.3)	(-1.1)	(-0.3)	(-1.1)	(-1.3)	(2.2)	(-1.1)	(7.3)	
(9)	35.8	41.5	49.7	65.3	49.7	41.5	35.8	37.1	25.2	37.1	35.8	41.5	37.1	49.7	
(9)	(-1.9)	(3.8)	(11.3)	(39.3)	(11.3)	(3.8)	(-1.9)	(-1.3)	(-0.8)	(-1.3)	(-1.9)	(3.8)	(-1.3)	(11.3)	
(9)	39.3	55.6	216.7	43.6	38.4	36.6	39.3	36.4	25.4	37.1	36.3	36.6	36.4	38.4	
(9)	(1.6)	(17.9)	(178.3)	(17.6)	(0.0)	(-1.1)	(1.6)	(-2.0)	(-0.6)	(-1.3)	(-1.4)	(-1.1)	(-2.0)	(0.0)	

<sup>a</sup> See note *a* in Table 1.

TABLE 3  
<sup>13</sup>C Chemical shifts and SCS (in parentheses) of mono-substituted triamantanes <sup>a</sup>

Compound	Carbon atom																		Other
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
(10a)	33.6	46.9	38.1	35.3	38.6	35.3	38.1	38.1	27.8	38.1	38.1	46.9	38.1	38.1	27.8	45.3	45.3	38.1	
(10b)	38.9	35.9	43.7	37.8	39.3	37.8	43.7	33.5	28.3	39.3	39.2	48.9	39.2	39.3	28.3	39.9	39.9	33.5	
(10c)	(5.3)	(-11.0)	(5.6)	(2.5)	(0.7)	(2.5)	(5.6)	(-4.6)	(0.5)	(1.2)	(1.1)	(2.0)	(1.1)	(1.2)	(0.5)	(-5.4)	(-5.4)	(-4.6)	
(10d)	38.1	73.7	44.1	39.6	38.1	39.6	44.1	32.7	27.5	38.1	38.1	49.7	38.1	38.1	27.5	39.4	39.4	32.7	
(10e)	(4.5)	(26.8)	(6.0)	(4.3)	(-0.5)	(4.3)	(6.0)	(-5.4)	(-0.3)	(0.0)	(0.0)	(2.8)	(0.0)	(0.0)	(-0.3)	(-5.9)	(-5.9)	(-5.4)	
(10f)	38.8	92.3	47.9	40.2	37.6	40.2	47.9	35.3	27.3	38.8	38.2	51.1	38.2	38.8	27.3	41.2	41.2	35.3	
(10g)	(5.2)	(45.4)	(9.8)	(4.9)	(-1.0)	(4.9)	(9.8)	(-2.8)	(-0.5)	(0.7)	(0.1)	(4.2)	(0.1)	(0.7)	(-0.5)	(-4.1)	(-4.1)	(-2.8)	
(10h)	37.7	77.0	36.9	39.3	38.3	39.3	36.9	32.3	27.5	38.4	38.1	49.9	38.1	38.4	27.5	39.3	39.3	32.3	
(10i)	(4.1)	(30.1)	(-1.2)	(4.0)	(-0.3)	(4.0)	(-1.2)	(-5.8)	(-0.3)	(0.3)	(0.0)	(3.0)	(0.0)	(0.3)	(-0.3)	(-6.0)	(-6.0)	(-5.8)	
(10j)	35.5	60.5	36.8	37.8	37.6	37.8	36.8	32.9	27.2	37.8	37.8	49.3	37.8	37.8	27.2	39.8	39.8	32.9	
(10k)	(1.9)	(13.6)	(-1.3)	(2.5)	(-1.0)	(2.5)	(-1.3)	(-5.2)	(-0.6)	(-0.3)	(-0.3)	(2.4)	(-0.3)	(-0.3)	(-0.6)	(-5.5)	(-5.5)	(-5.2)	
(10l)	33.9	51.5	34.7	40.0	33.9	35.7	32.6	38.3	27.9	38.1	38.1	46.9	38.9	38.3	29.0	45.5	45.5	47.2	
(10m)	(0.3)	(4.6)	(-3.4)	(4.7)	(-4.7)	(0.4)	(-5.5)	(0.2)	(0.1)	(0.0)	(0.0)	(0.0)	(0.8)	(0.2)	(1.2)	(0.2)	(0.5)	(9.1)	
(10n)	35.9	52.0	71.0	39.7	32.8	34.6	30.7	37.6	27.5	37.6	37.3	45.9	41.0	37.2	32.0	44.6	44.6	46.1	
(10o)	(2.3)	(5.1)	(32.9)	(4.4)	(-5.8)	(-0.7)	(-7.4)	(-0.5)	(-0.3)	(-0.5)	(-0.8)	(-1.0)	(2.9)	(-0.9)	(4.2)	(-0.7)	(-1.0)	(8.0)	
(10p)	38.9	55.0	79.9	44.1	35.5	34.7	34.4	37.6	27.3	37.6	38.1	45.9	41.8	37.3	32.5	44.5	44.5	51.7	
(10q)	(5.3)	(8.1)	(41.8)	(8.8)	(-3.1)	(-0.6)	(-3.7)	(-0.5)	(-0.2)	(-0.5)	(0.0)	(-1.0)	(3.7)	(-0.8)	(4.7)	(-0.8)	(-0.4)	(13.6)	
(10r)	34.0	46.3	38.0	35.4	38.3	34.6	39.0	45.2	29.6	45.2	39.0	46.3	38.0	38.3	27.9	45.4	45.4	38.3	
(10s)	(0.4)	(-0.6)	(-0.1)	(0.1)	(-0.3)	(-0.7)	(0.9)	(7.1)	(1.8)	(7.1)	(0.9)	(-0.6)	(-0.1)	(0.2)	(0.1)	(0.1)	(7.2)	(0.2)	
(10t)	35.9	45.7	37.4	35.0	37.6	34.0	40.6	45.5	68.2	45.5	40.6	45.7	37.4	38.0	27.1	45.0	45.0	38.0	
(10u)	(2.3)	(-1.2)	(-0.7)	(-0.3)	(-1.0)	(-1.3)	(2.5)	(7.4)	(40.4)	(7.4)	(2.5)	(-1.2)	(-0.7)	(-0.1)	(-0.7)	(-0.3)	(7.4)	(-0.1)	
(10v)	38.1	45.2	37.3	34.6	37.5	33.6	42.2	49.7	65.5	49.7	42.2	45.2	37.3	37.7	27.0	44.7	44.7	37.7	
(10w)	(4.5)	(-1.7)	(-0.8)	(-0.7)	(-1.1)	(-1.7)	(4.1)	(11.6)	(37.7)	(11.6)	(4.1)	(-1.7)	(-0.8)	(-0.4)	(-0.8)	(-0.6)	(11.2)	(-0.4)	

<sup>a</sup> See note *a* in Table 1. Shifts marked by \*, †, or ‡ may be interchanged.

assignments of the <sup>13</sup>C signals of the remaining 1- and 2-substituted adamantanes were straightforward and follow those already published.<sup>3-5</sup> The signals of 2-methyl- (3c) and 2-phenyl-adamantan-2-ol (4c) were assigned with the help of europium induced shifts. Thus the data of the two  $\gamma$ - and the two  $\delta$ -carbon atoms of (3c) reported recently<sup>11</sup> had to be reversed pairwise. The  $\delta$ -signals of the corresponding bromo derivatives (3d) and (4d) were assigned analogously, but the two  $\gamma$ -signals of (4d) were so close together that no safe assignment was possible. The peak assignment of (5c and d) were made using different signal intensities due to the symmetry of the molecule. The data of (5c) agree with those reported earlier.<sup>11</sup>

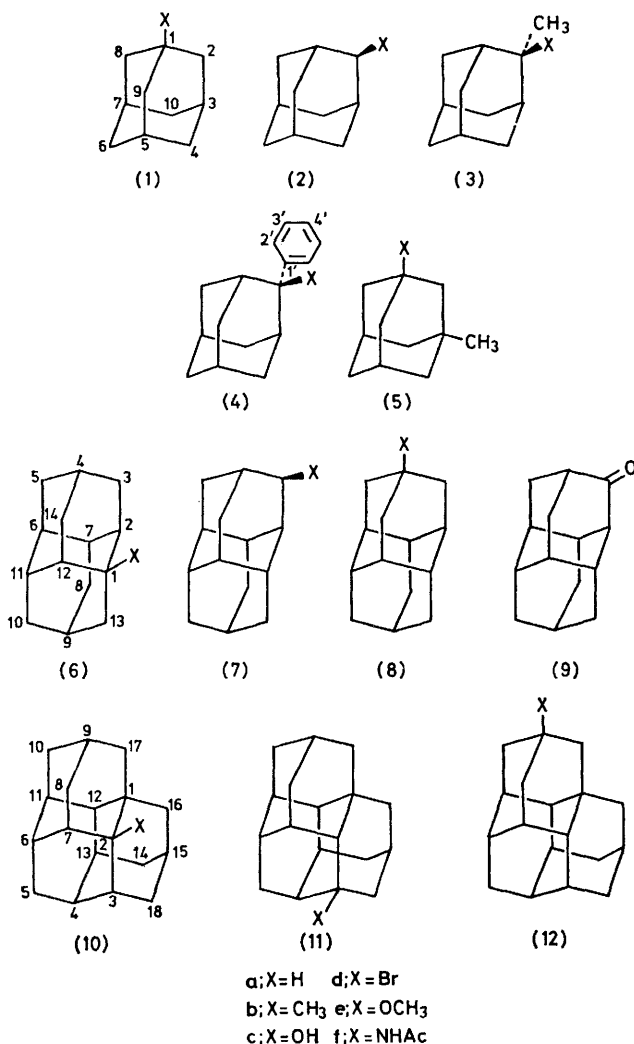
The 1-substituted adamantanes (6b—d) give rise to 10 carbon signals which can easily be assigned making use of their different intensities. Signals for carbon atoms with the same number of adjacent hydrogen atoms and representing equal numbers of equivalent carbons

were differentiated by comparison with calculated chemical shifts obtained by adding SCS from 1- and 2-substituted adamantanes to the chemical shifts of adamantane in an appropriate manner.

Similarly, the chemical shifts of 3-methyl- (7b), 3-hydroxy- (7c), and 3-bromo-diamantane (7d) and diamantanone (9) were assigned by comparing them with the calculated chemical shifts utilizing SCS from (2b—d) and adamantane.<sup>5</sup> Some of the assignments are ambiguous (*cf.* Table 2), but these mostly concern remote carbon atoms and the differences of the SCS caused by interchanging the chemical shifts are small. The assignment of the 4-substituted adamantanes (8b—d) was straightforward also; due to their C<sub>3v</sub> symmetry their spectra show only six lines which can easily be attributed to the corresponding carbon atoms by considering their intensities and comparing the SCS with those of the 1-substituted adamantanes (1b—d).

Due to their symmetries the 2-, 3-, and 9-substituted

triamantanes show 11, 18, and 13 signals, respectively, in their  $^{13}\text{C}$  n.m.r. spectra. The assignment is again based on relative intensities and calculated chemical shifts obtained by addition of SCS from monosubstituted adamantanes and/or diamantanes to the chemical shifts of triamantane.<sup>1</sup> Ambiguities only occur for 3-substituted triamantanes and are negligible except for C-9 and -15 of (11b) (*cf.* Table 3). Additionally, the assignment of (10c) was verified by spectra measured in the presence of  $\text{Yb}(\text{dpm})_3$ ; superimposed signals were detected by changing the solvent.



## RESULTS AND DISCUSSION

**$\alpha$ -Effects.**—The  $\alpha$ -SCS for certain substituents vary drastically in the different molecules, *e.g.* the hydroxy group can cause a downfield shift of 41.5 p.p.m. in diamantan-4-ol (8c) or of 26.8 p.p.m. in triamantan-2-ol (10c). Analogously,  $\alpha$ -bromo effects of 45.4 and 25.9 p.p.m. and  $\alpha$ -methyl effects of 1.8 and even -11.0 p.p.m. can be found. The latter value, with the possible exception of that for the iodo substituent, is, to our knowledge, the largest shielding  $\alpha$ -effect ever recorded.

Recently, Beierbeck and Saunders<sup>12,13</sup> published a method of estimating  $^{13}\text{C}$  chemical shifts of saturated hydrocarbons. They found that for staggered conformations the  $^{13}\text{C}$  chemical shifts can be calculated by addition of basic  $\alpha$  shifts, exocyclic C-C, X-C, and H-C gauche interactions and non-bonded  $\gamma$ - and  $\delta$ -increments to the chemical shifts of certain parent hydrocarbons.<sup>12,13</sup> The application of their method to the methyl and hydroxy compounds in our study led to fairly good results if the chemical shifts of the parent diamondoid hydrocarbon (X = H) are taken as a basis. It turns out that for bridgehead substituted compounds the large differences of the  $\alpha$ -SCS are mainly caused by the varying number of gauche interactions (XC)\* between the substituent X and  $\gamma$ -carbon atoms (*cf.* Figure 1). The gauche interaction XC replaces an interaction of a  $\gamma$ -carbon atom with the hydrogen atom at the  $\alpha$ -carbon atom (HC) so that the net contribution from the X-C interactions is (XC-HC).<sup>13</sup> In the compounds (1), (5), (8), and (12) no (XC-HC) interaction is present, whereas for (3), (6), and (11) two and for (10) four are found. From the data in Table 4 the numerical values of the

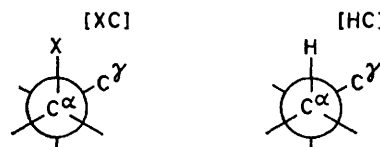


FIGURE 1

(XC-HC) contributions can roughly be estimated: (CC-HC) = -3 ( $\pm$  ca. 1), (OC-HC) = -3.3 ( $\pm$  ca. 0.5), (BrC-HC) = +1.9 ( $\pm$  ca. 0.5) p.p.m. Beierbeck and Saunders<sup>12,13</sup> reported for (CC-HC) -2.99 and for (OC-HC) -2.29 p.p.m. so that a qualitative sequence of the magnitude of the XC interactions can be deduced: BrC > HC > CC  $\approx$  OC. This allows us to state that the X-C gauche interactions are governed neither by the electronegativity of X nor by steric repulsion.

TABLE 4

$\alpha$ -SCS of bridge-head substituted diamondoid hydrocarbons

	Number of XC interactions		
	0	2	4
CH <sub>3</sub>	1.2; 1.7 1.8	-3.7 -3.4	-11.0
OH	40.0; 39.4 41.5; 40.4	34.6; 33.1 32.9	26.8
Br	36.8; 38.0 39.3; 37.7	43.1; 41.4 41.8	45.4

The data of (4c and d) were excluded in this context, since additional remarkable contributions to the  $\alpha$ -SCS, probably due to direct interaction between the phenyl ring and X, must be taken into consideration.

**$\beta$ -Effects.**—The main contributions governing the  $\beta$ -SCS are again gauche interactions.<sup>12,13</sup> But in contrast to the  $\alpha$ -SCS two different types of gauche interactions now have to be taken into account (Figure 2).<sup>12,13</sup>

\* The abbreviations for the gauche interactions are those given in the refs. 12 and 13.

Since the numerical values of the two interaction mechanisms are different and  $HX > CX$ ,<sup>12,13</sup> the  $\beta$ -SCS values become larger with an increasing number of HX interactions, *i.e.* of hydrogen atoms attached to the  $\beta$ -carbon atoms. All  $\beta$ -SCS values are listed in Table 5.

TABLE 5

$\beta$ -Carbon atom HX/CX	$\beta$ -SCS of diamondoid hydrocarbons		
	C 0/2	CH 1/1	CH <sub>2</sub> and CH <sub>3</sub> 2/0
X = CH <sub>3</sub>	5.3	3.4; 4.5; 4.6 4.7; 5.5; 5.6 5.6	6.8; 7.1; 7.1 7.2; 8.6; 8.8 9.1
X = OH	4.5	4.4; 5.1; 5.3 5.7; 6.0; 6.2 6.2; 6.4	7.3; 7.4; 7.4 7.5; 7.6; 7.7 8.0; 8.0; 8.6
X = Br	5.2	7.5; 8.0; 8.1 8.1; 8.2; 8.5 8.8; 9.8	11.2; 11.3; 11.3 11.5; 11.6; 11.6 13.3; 13.6; 13.9

Although the number of examples is too small to allow quantitative evaluations, the following trends can be observed: the magnitude of the differences in the  $\beta$ -SCS are relatively larger for X = Br and smaller for X = CH<sub>3</sub> and OH. An inspection of the data in Table 5 shows

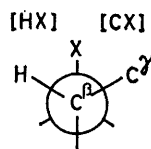


FIGURE 2

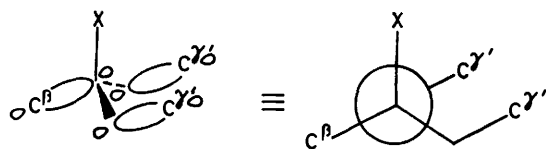


FIGURE 3

that the CX values are apparently similar for all three substituents. The reported values<sup>12,13</sup> for CC and CO are 1.74 and 2.27 p.p.m., respectively. Also the HO and HC values seem to be similar (HC 4.73<sup>12</sup> and HO 4.42 p.p.m.<sup>13</sup>); the HBr value, however, appears to be significantly larger.

In addition to the gauche interaction a second contribution affects the  $\beta$ -SCS: for each substituent the compounds with the same combinations of HX and CX can be arranged into two groups (*cf.* Table 5). If there are  $\gamma$ -carbon atoms which are antiperiplanar to the  $\beta$ -carbon atom, the  $\beta$ -SCS are somewhat larger (1–2 p.p.m.) than in molecules without such antiperiplanar  $\gamma'$ -carbon atoms. This may be explained by a delocalization of the charge polarization at the  $\beta$ -carbon atom *via* an interaction of the  $C_\alpha-C_\beta$  with the parallel  $C_{\beta'}-C_{\gamma'}$  bond orbital (*cf.* Figure 3).

This seems to be valid generally only for the bridgehead substituted compounds. The  $\beta$ -SCS of the tertiary alcohols (2c) and (7c) and the related methyl compounds (2b) and (7b) are large, although no antiperiplanar  $\gamma'$ -carbon atoms are present. The corresponding bromo

derivatives (2d) and (7d), however, show small  $\beta$ -SCS values.

$\gamma_{syn}$ -Effects.—The shielding substituent effects on gauche  $\gamma$ -carbon atoms are diagnostically the most valuable SCS. Since the pioneering work of Grant and Cheney<sup>14</sup> this shielding effect has been attributed to a through-space interaction of the substituent X and the syn-axial hydrogen atom at the gauche  $\gamma$ -carbon atom. Recently, however, Beierbeck and Saunders<sup>15</sup> reported an interesting new interpretation of the  $\gamma_{syn}$  SCS, implying that the upfield shift of a gauche  $\gamma$ -carbon atom is due to the replacement of the hydrogen atom at the  $\alpha$ -carbon atom by X and that a shielding effect of steric compression does not exist.

The  $\gamma_{syn}$  SCS in this study do not behave similarly for all three substituents. For the methyl compounds (2b), (3b), (6b), (7b), (10b), and (11b) they vary between –4.6 and –6.3 p.p.m., and no dependence on the substitution pattern at the  $\alpha$ -,  $\beta$ -, or  $\gamma_{syn}$ -carbon atom can be detected. For the alcohols (2c)–(4c), (6c), (7c), (10c), and (11c) the  $\gamma_{syn}$  SCS are uniformly *ca.* –6 p.p.m. The only exception (–7.4 p.p.m.) occurs at the methine C-7 of (11c). A similar observation was reported recently by Djerassi *et al.*<sup>16</sup> The bromides (2d)–(4d), (6d), (7d), (10d), and (11d), however, show a significant trend. If the  $\alpha$ -carbon atom is methine [(2d) and (7d)], the  $\gamma_{syn}$ -SCS are *ca.* –6 p.p.m.; but if it is quaternary [(3d), (4d), (6d), (10d), and (11d)], the upfield shifts apparently decrease with increasing steric crowding around the  $C_\alpha$ -Br moiety. For example in (3d) the  $\gamma_{syn}$ -SCS is –5.0, in (4d) *ca.* –4, and in (10d) only –4.1 (C-16, -17) and –2.8 p.p.m. (C-8, -18). This corresponds to the observation<sup>17</sup> that the introduction of a second bromine atom into 2-bromoadamantane forming 2,2-dibromoadamantane causes upfield shifts of only –2.7 p.p.m. for the signals of the carbon atoms which are in the gauche  $\gamma$ -position relative to the second bromo substituent.

Since this dependence of the  $\gamma_{syn}$  shifts on the substitution pattern only exists for the bromo, but not for the methyl and the hydroxy compounds, it cannot originate in inductive effects so that we were led to the conclusion that, on the basis of Beierbeck and Saunders' interpretation,<sup>15</sup> steric compression causes downfield rather than upfield shifts. This was already observed earlier for  $\delta$ -carbon atoms:<sup>18,19</sup> whereas the  $\delta$ -SCS generally seem to be slightly negative,<sup>3,4</sup> those for syn-axial carbon atoms in the  $\delta$ -position are positive.<sup>18</sup> This cannot be explained by the fact that the syn-axial  $\delta$ -carbon atom replaces the syn-axial hydrogen atom at the  $\gamma$ -carbons atom, *i.e.* that a small upfield shift replaces a larger one resulting in a net downfield shift,<sup>20</sup> because an interaction of the syn-axial hydrogen atom and X is not the cause of the shielding  $\gamma$ -effects.<sup>15</sup>

$\gamma_{anti}$ -Effects.—In a recent survey Eliel *et al.*<sup>21</sup> reported that for primary and secondary alcohols, amines, and fluorides the substituents induce upfield shifts at anti-periplanar carbon atoms. For bridgehead substituted compounds these  $\gamma_{anti}$ -SCS seem to be generally posi-

tive.<sup>3,4,22,23</sup> Wiseman *et al.*<sup>24</sup> showed that downfield  $\gamma_{anti}$ -SCS of hydroxy substituents are not due to the fact that the  $\alpha$ -carbon atoms are at bridgeheads, but that they are quaternary atoms. This is confirmed by our data in this and in a previous study.<sup>17</sup>

Eliel *et al.*<sup>21</sup> proposed a hyperconjugative mechanism for the interaction of lone electron pairs of the hetero substituents with an antiperiplanar  $\gamma$ -carbon atom (Figure 4). In a previous study<sup>25</sup> we described two

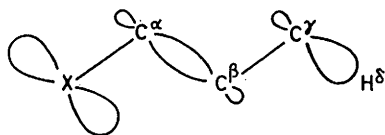


FIGURE 4

different dependences of the  $\gamma_{anti}$ -SCS of hetero substituents. (a) The downfield  $\gamma_{anti}$ -SCS decreases, if the atoms concerned ( $X-C_\alpha-C_\beta-C_\gamma-H_\delta$ ) are distorted out of the coplanar arrangement.<sup>25</sup> Analogous results were observed simultaneously for substituted twistanes,<sup>8</sup> and also the  $\gamma_{anti}$ -SCS reported for norcaranes<sup>26</sup> fit this mechanism. (b) The downfield  $\gamma_{anti}$ -SCS of hetero substituents increase, if the coplanar atoms, X,  $C_\alpha$ ,  $C_\beta$ ,  $C_\gamma$ , and  $H_\delta$  are compressed within the plane.<sup>25</sup> An inspection of the  $\gamma_{anti}$ -SCS at C-3 of (5c and d) and of those at C-1 of (12c and d) reveals that the former are larger than the latter for each substituent, although in both systems the coplanar  $\delta$ -atoms are carbon. This is caused by the fact that the bond angle between C-16, -1, and -17 in (12c and d) is expected to be unusually large<sup>1,27</sup> due to a pairwise repulsion of the syn-diaxial hydrogens at C-16 and -17 (*cf.* Figure 5a). In (5c and d),

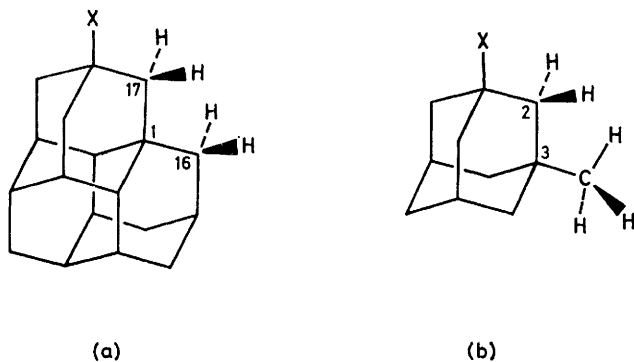


FIGURE 5

however, the methyl group can rotate freely and thus escape steric interaction so that the corresponding angle between  $CH_3$ , C-3, and -2 should be nearly tetrahedral (*cf.* Figure 5b). According to the above mechanism the expansion of the molecular arrangement in question in the triamantanes (12c and d) causes a decrease of the  $\gamma_{anti}$ -SCS. (c) Comparing the  $\gamma_{anti}$  hydroxy SCS of adamantan-1-ol (1c), the tertiary diamantanols (6c) and (8c), and the triamantanols (10c)—(12c), a third contribution to this substituent effect can be deduced.

By analogy with the  $\beta$ -SCS, the  $\gamma_{anti}$ -SCS are increased if  $\gamma'$ -carbon atoms antiperiplanar to the  $\beta$ -carbon atoms are present. Again the charge polarization may be perturbed by a hyperconjugative interaction of the  $C_\alpha-C_\beta$  and the  $C_\beta-C_{\gamma'}$  bond orbitals. This is exemplified with diamantan-1-ol (6c) (Figure 6). There are two different hydroxy  $\gamma_{anti}$ -SCS: 4.5 at C-9 and 2.3 p.p.m. at C-7. The larger effect at C-9 is caused by the presence of C-3 and -14 which are antiperiplanar to C-13, whereas C-2 has no antiperiplanar carbon atoms so that the hydroxy  $\gamma_{anti}$ -SCS at C-7 is smaller. Apparently, this mechanism is less effective for the bromides although an analogous trend can also be recognized; possibly due to the size of the bromine atom structural distortions involving contributions (a) and/or (b) play a significant part here also.

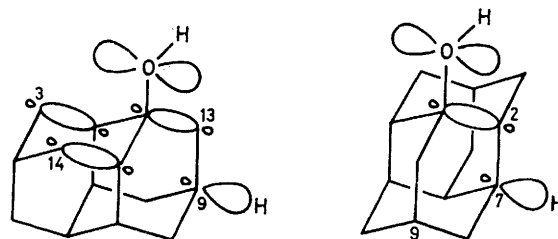


FIGURE 6

(d) The differences in the  $\gamma_{anti}$ -effects in (5c and d) (those at C-3 are larger than those at C-5 and -7) may be caused by the fact that the  $C_\gamma-Y_\delta$  bond orbitals are of different nature. It is a C-H bond orbital ( $2sp^3-1s_H$ ) in the C-5 and -7 case and a C-C bond orbital ( $2sp^3-2sp^3$ ) in the C-3 case. Due to the lack of examples with coplanar  $\delta$  carbon atoms it cannot yet be confirmed whether the nature of the  $C_\gamma-Y_\delta$  ( $Y = H$  or C) has such a pronounced effect. If Y is a halogen, the  $\gamma_{anti}$ -SCS differ remarkably from those with  $Y = H$ ,<sup>6</sup> but these examples cannot be compared, since the halogen atoms themselves have lone pairs and further electronic interactions between the halogen atoms X and Y must be considered.<sup>6</sup>

The methyl  $\gamma_{anti}$ -SCS are small and mostly negligible. This is expected on the basis of the hyperconjugative interaction model, since the methyl group does not have a lone electron pair.

*Effects on Remote Carbon Atoms.*—The  $\delta$ -SCS are in the range  $-2.1$  to  $+2.2$  p.p.m., and the more distant carbon atoms ( $\epsilon$  and  $\zeta$ ) do not exhibit appreciable substituent effects.

In the 2-substituted 2-phenyladamantanes (4c and d) the OH and Br SCS at the aromatic carbon signals are remarkable. The  $\beta$ -effects on C-1' are only 1.6 and 1.4 p.p.m., respectively, the  $\gamma$ -effects on the *ortho*-carbon atoms are slightly negative and the  $\delta$  effects on the *meta*-carbon atoms 1.0 p.p.m. in both cases. The  $\epsilon$  effects on the *para*-carbon atoms, however, are surprisingly high,  $+2.5$  and  $+2.6$  p.p.m., respectively. This must be attributed to a direct through-space interaction of the substituents with the phenyl ring.

## EXPERIMENTAL

Monosubstituted adamantanes not mentioned in previous papers were prepared as follows. The methyladamantanes (1b) and (2b) were obtained by reduction of the corresponding acid with  $\text{LiAlH}_4$  to the primary alcohols, subsequent tosylation and again reduction with  $\text{LiAlH}_4$ . The methoxy derivatives (1e) and (2e) were prepared by methylation of the corresponding alcohols with  $\text{NaH-CH}_3\text{I}$  and the acetamides (1f) and (2f) by acetylation of the commercially available amines with acetic anhydride. The quaternary alcohols (3c) and (4c) were prepared by Grignard reactions with adamantanone using  $\text{CH}_3\text{MgI}$  and  $\text{C}_6\text{H}_5\text{MgBr}$ , respectively. The corresponding bromides (3d) and (4d) were obtained by reaction of the alcohols (3c) and (4c) with 48%  $\text{HBr}$  in  $\text{CCl}_4$ . Compound (4a) was prepared by Wolff-Kishner reduction of 4-phenyladamantanone.<sup>28</sup> Compound (5d) was obtained by bromination of (1b)<sup>29</sup> and (5c) by hydrolysis of (5d).<sup>29</sup> The preparation of the diamantanes<sup>30</sup> and triamantanes is described elsewhere.<sup>31</sup>

The  $^{13}\text{C}$  n.m.r. spectra were recorded at 22.64 MHz in  $\text{CDCl}_3$  solution using a Bruker WH-90 spectrometer. The chemical shifts are referred to tetramethylsilane; positive values correspond to downfield shifts.

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