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^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA—VI

STEREOCHEMICAL DEPENDENCE OF γ_{anti} HETEROSUBSTITUENT EFFECTS ON ^{13}C CHEMICAL SHIFTS OF BRIDGEHEAD SUBSTITUTED MOLECULES[1]

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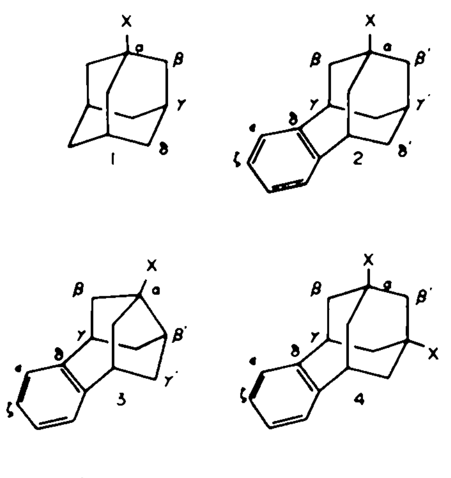
Abstract—The ^{13}C NMR data of some mono- and disubstituted adamantanes, homoadamantenes and homonoradamantenes are presented. A model of dependencies of the γ_{anti} substituent induced shifts on torsion angles and internuclear distances between substituents and the γ carbons is proposed. Furthermore, it is shown that for the α substituent induced shifts strain within the molecular frameworks of these compounds plays no significant part.

During the last few years ^{13}C NMR spectroscopy has achieved increasing importance for organic chemists, since it was realized that the ^{13}C shielding and the coupling between carbons and other nuclei are strongly dependent on even minor changes of the geometrical and electronic environments of organic molecules.[2-6] A variety of empirical rules for the estimation of ^{13}C chemical shifts has been established which are derived from experimental data. But nevertheless, the carbon shielding and its dependence on various influences is not yet well understood and it is still impossible to predict unknown chemical shifts with fairly good accuracy in all cases.

Recently, Maciel presented a compilation of substituent effects known in literature.[7] Following his approach, it may sometimes be a great problem to separate particular contributions to the substituent effects and to obtain experimental data for each of them. To that end investigations of conformationally rigid molecules with well defined configurations are most welcome, e.g. norbornanes,[8-10] adamantanes,[11-14] steroids[15,16] and other polycyclic frameworks.



	a	b	c	d	e	f	g
X =	H	OH	Cl	Br	I	OCH_3	$OCOCH_3$

Scheme 1. Compound structures.

In this study the ^{13}C NMR data of benzohomoadamantenes (series **2** and **4**) and benzohomonoradamantenes (series **3**) are presented. All these molecules are totally rigid, but they are more or less strained. The various arrangements of substituents, carbons and hydrogens differ, at least in part, considerably from the staggered configurations of adamantane molecules (series **1**) they will be compared with in order to find out stereochemical dependencies of the substituent chemical shifts (SCS).

RESULTS

Monosubstituted compounds (*series* **1**–**3**).

Assignment. The ^{13}C NMR signals were assigned with the aid of substituent effects known from 1-substituted adamantanes and using spectra obtained under partial proton decoupling conditions ("off-resonance"). Signals providing equal multiplicities in the off-resonance spectra could be assigned via their different intensities. Since all compounds involved have at least one mirror plane, the intensities of signals associated to more than one equivalent carbons correspond fairly well to the respective number of these carbons.

The data of 1-substituted adamantanes are similar to those reported by Lippmaa *et al.*[11] and Maciel *et al.*[12] considering the differing concentrations and solvents.

The signals of the ϵ and ζ carbons of the unsubstituted compounds **2a** and **3a** were assigned by applying the "finger-print-rule" for undecoupled spectra proposed by Günther *et al.*[17] Because the substituent effects upon these carbons are expected to be rather small, the signals of the ϵ and ζ carbons of the substituted derivatives are assigned analogously. The coupling constants $^1J_{CH}$ obtained from the undecoupled spectra are different, being 154–155 Hz for the ϵ and 158–160 Hz for the ζ signal.

DISCUSSION

γ *Effects.* Today negative γ SCS, i.e. upfield shifts induced by substituents, are agreed to arise from steric interaction between the substituent and a hydrogen at the γ positioned carbon.[2,3,7,8,18] This interaction is only conceivable, if the substituent is gauche positioned relative to the γ carbon.

Often, this interaction is thought to be a steric repul-

Table 1. ^{13}C chemical shifts of 1-substituted adamantanes and monosubstituted homoadamantenes and homonoradamantenes; substituent chemical shifts (SCS) in parentheses[a]

	α	β	β'	γ	γ'	δ	δ'	ε	ζ
1a	28.5	37.8	--	28.5	--	37.8	--	--	--
1b	67.9 (39.4)	45.3 (7.5)	--	30.8 (2.3)	--	36.1 (-1.7)	--	--	--
1c	68.2 (39.7)	47.7 (9.9)	--	31.7 (3.2)	--	35.6 (-2.2)	--	--	--
1d	66.5 (38.0)	49.4 (11.6)	--	32.6 (4.1)	--	35.7 (-2.1)	--	--	--
1e	50.2 (21.7)	52.3 (14.5)	--	32.9 (4.4)	--	35.5 (-2.3)	--	--	--
2a	28.8	35.6	36.4	41.6	28.8	148.1	35.6	128.1	125.9
2b	68.8 (40.0)	43.5 (7.9)	44.4 (8.0)	41.8 (0.2)	33.1 (4.3)	146.5 (-1.6)	34.2 (-1.4)	128.1 (0.0)	126.3 (0.4)
2c	69.9 (41.1)	45.6 (10.0)	46.9 (10.5)	43.0 (1.4)	33.7 (4.9)	146.0 (-2.1)	33.8 (-1.8)	128.2 (0.1)	126.6 (0.7)
2d	68.1 (39.3)	46.9 (11.3)	48.2 (11.8)	43.8 (2.2)	34.1 (5.3)	145.9 (-2.2)	33.6 (-2.0)	128.1 (0.0)	126.5 (0.6)
2e	52.9 (24.1)	49.9 (14.3)	51.1 (14.7)	44.7 (3.1)	33.9 (5.1)	145.9 (-2.2)	33.5 (-2.1)	128.0 (-0.1)	126.5 (0.6)
2f[b]	72.4 (43.6)	39.0 (3.4)	41.2 (4.8)	41.6 (0.0)	32.8 (4.0)	146.7 (-1.4)	34.6 (-1.0)	128.1 (0.0)	126.4 (0.5)
2g[c]	81.4 (52.6)	39.3 (3.7)	41.0 (4.6)	41.8 (0.2)	33.0 (4.2)	146.4 (-1.7)	34.4 (-1.2)	128.1 (0.0)	126.4 (0.5)
3a	42.9	43.7	42.9	49.0	43.7	146.4	--	129.3	125.6
3b	90.3 (47.4)	50.9 (7.2)	49.5 (6.6)	48.2 (-0.8)	42.7 (-1.0)	145.1 (-1.3)	--	129.3 (0.0)	126.1 (0.5)
3c	78.9 (36.0)	53.6 (9.9)	53.0 (10.1)	48.6 (-0.4)	42.4 (-1.3)	144.4 (-2.0)	--	129.3 (0.0)	126.2 (0.6)
3d	70.6 (27.7)	54.9 (11.2)	54.0 (11.1)	48.7 (-0.3)	42.2 (-1.5)	144.0 (-2.4)	--	129.0 (-0.3)	126.1 (0.5)
3e	46.9 (4.0)	58.1 (14.4)	57.1 (14.2)	49.1 (0.1)	41.8 (-1.9)	144.1 (-2.3)	--	128.9 (-0.4)	126.0 (0.4)

[a] The chemical shifts are given relative to tetramethylsilane. Positive values correspond to deshielding.

[b] CH_3: 47.8 ppm.

[c] CH_3: 22.7 ppm; C = O: 170.0 ppm.

sion. This interpretation, however, should be avoided, because there is evidence that there is no essential steric repulsion between a monoatomic substituent and a hydrogen both being in 1,3-diaxial configuration, e.g. an X-ray study of 2-iodoadamantane[19] showed that there is no significant distortion of the molecular geometry of the adamantane framework. Very recently,[16c] Beierbeck and Saunders presented a new interpretation of the γ_{syn} effect which denies that steric interaction between a substituent X and a γ hydrogen is the reason for the upfield shift at all.

Other possibilities of configurations, e.g. the substituent being antiperiplanar to the γ carbon, are not well investigated. Only for the second-row substituents (N, O, F) not fixed at a bridgehead carbon is there a detailed study[20] showing that a substituent of this type induces an upfield shift at a antiperiplanar γ carbon which is even larger than at a corresponding gauche carbon.

Often however, and particularly in cases excluded in Ref. 21, downfield SCS at γ carbons are observed. The γ increments of the compounds presented in this study are mostly positive or about zero. Astonishingly, the average of the two different γ shifts at the homoadamantene derivatives matches nearly exactly the corresponding γ shift at the adamantanes for all different substituents, the γ' SCS being larger and the γ SCS being smaller. Only the γ' shifts of the homonoradamantenes (series 3) are slightly negative (−1.0 to −1.9 ppm). Indeed, this is the only arrangement which differs significantly from an antiperiplanar configuration, and a steric interaction between the substituent and the hydrogen at the γ' carbon is at least conceivable.

In Fig. 1 the γ SCS of the various bromo derivatives are plotted versus the distance r between the bromine and the next γ hydrogen nuclei in each case. For comparison reasons the γ_{syn} SCS of 2-bromoadamantane[13] was added. Although this compound is not a tertiary but a secondary bromide this increment gives a idea of a γ

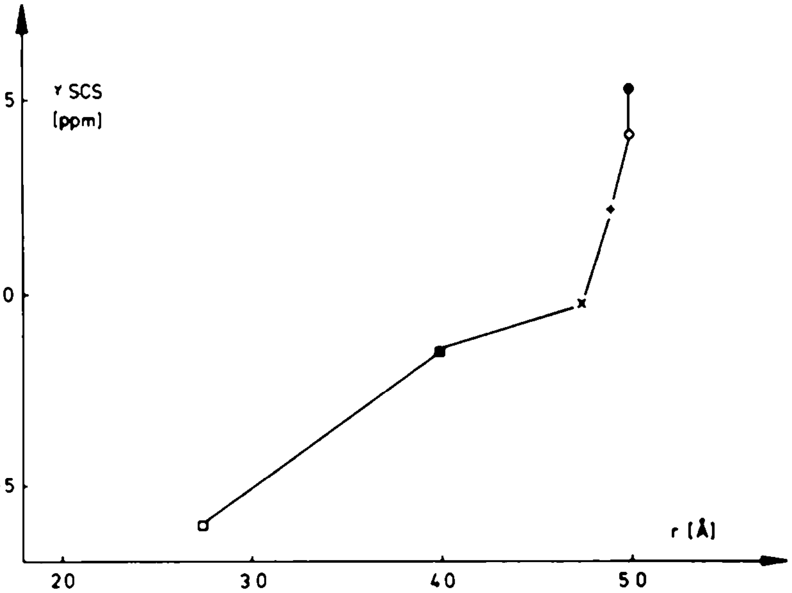


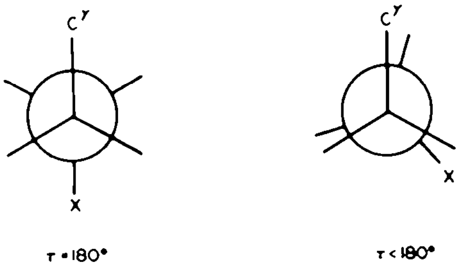
Fig. 1. Substituent effects upon the γ positioned carbons (γ SCS) versus the distances between the bromine atom and the next hydrogen nuclei (●: γ' SCS of **2d**; ○: γ SCS of **1d**; +: γ SCS of **2d**; ×: γ SCS of **3d**; ■: γ' SCS of **3d** and □: γ_{syn} SCS of 2-bromoadamantane).

shift induced by a gauche bromine substituent. The internuclear distances in Fig. 1 are estimated from Dreiding models.

The other substituents (OH, Cl and I) show similar figures.

The diamagnetic SCS decrease with increasing internuclear distance. At large distances (4.7–5.0 Å) the increments become positive and cover a range of about 5 ppm. This points to the fact that there are at least two interaction mechanisms leading to diamagnetic and to paramagnetic γ effects.

Looking at the models it can be realized that several of the X–C^{α}–C^{β}–C^{γ} arrangements show deviations from coplanarity (torsion angle $\tau = 180°$). There are configurations with the substituent X distorted from the plane formed by the three carbons, thus decreasing the torsion angles:



$\tau = 180°$

$\tau < 180°$

Fig. 2

These angles are 180° for the adamantanes and the γ' carbons of the homoadamantenes, of course, because in these cases all atoms concerned are located in a symmetry plane of the molecule. However, for the γ carbons of the homoadamantenes this angle is about 170°, and for the homonoradamantenes angles of 145° for the γ carbons and 125° for the γ' carbons are determined. All these values are roughly estimated, because the model cannot reflect the true molecular geometry exactly. Therefore a deviation of a few degrees must be accepted. An inspectrion of the various γ increments shows that the smaller the torsion angle τ, i.e. the larger the deviation from coplanarity, the smaller are the paramagnetic shifts of the signals in question for an individual substituent.

In Fig. 3 the γ SCS of the various substituted compounds of the series **1**, **2** and **3** are plotted versus the sine function of the torsion angle τ.† We suppose that the angular dependence of the downfield γ SCS in antiperiplanar configuration can be described by the follow-

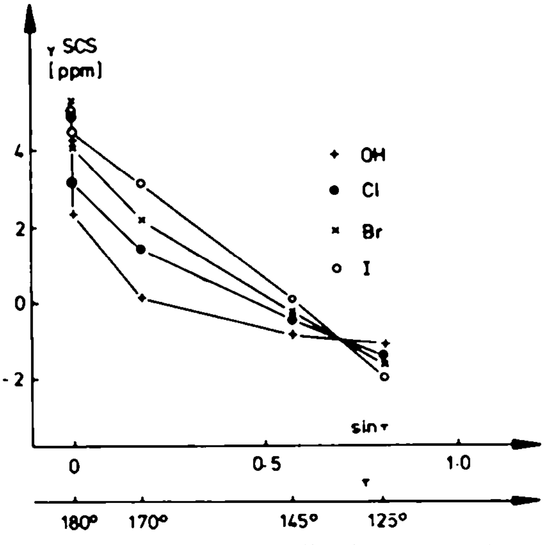


Fig. 3. γ Substitutent chemical shifts of the various adamantanes, homoadamantenes and homonoradamantenes (see text) versus the sine of the torsion angles (sin τ).

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†One referee pointed out that the sine is an unusual function in this context. Of course, we are aware that every M.O. theory relates substituent effects to cosine dependences. But nevertheless, we want to report this surprising sin φ dependence by which this γ_{anti} effect can be described, although we cannot give theoretical explanations so far.

ing expression:

$$\gamma\,\mathrm{SCS} = -A \sin \tau + B. \qquad (1)$$

The good accordance of the experimental data for X = I with eqn (1) is becoming worse with the decreasing size of the substituents. The curves bend towards the horizontal direction when the increments are approaching the value zero for the γ SCS. This indicates that at least in this region the γ effect can no longer be described by only one mechanism. With small deviations from coplanarity the slopes are approximately the same for all four substituents. Thus A in eqn (1) seems to be an intrinsic factor of the downfield effect, more or less independent of the substituents' character. B, however, is associated with the substituents themselves and decreases in the series I, Br, Cl and OH, i.e. downfield shifts induced by iodo substituents are larger than those induced by bromo substituents, etc.

Comparing the γ SCS of 1-substituted adamantanes with those of 1-substituted bicyclo[2.2.2]octanes[1] (X = OH: −0.2; X = Cl: 1.0; X = Br: 1.9; X = I: 2.5 ppm) it is observed that the downfield shifts of the latter compounds are about 2-2.5 ppm smaller than the corresponding ones of the adamantanes. This seems to contradict the description of the γ effects outlined above, since the conformation of the bicyclooctanes with D_{3h}-symmetry is totally eclipsed and the four atoms X, C^α, C^β and C^γ are coplanar again. However, the bicyclooctanes cannot be regarded as rigid but as swinging molecules.[21] They are mixtures of both enantiomers with D_3-symmetry which are separated by a small energy barrier (Fig. 4).

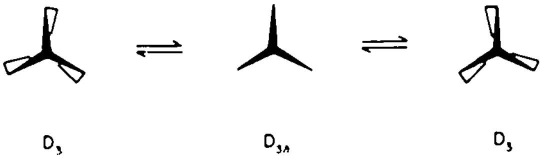
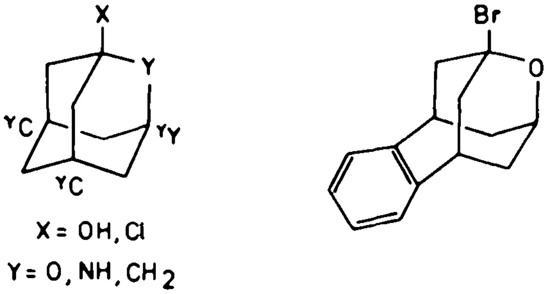


Fig. 4.

Even Dreiding models reveal the flexibility of these molecules, and it was reported[21] that they can be distorted up to 12° without any significant changes of bond lengths. This indicates that the weighted average of all conformations has a certain distortion angle φ, thus producing a deviation from coplanarity of the atoms of interest and giving reduced downfield shifts.

The concept of an angular dependent downfield γ SCS, of course, cannot explain discrepancies of γ_{anti} effects occurring at different molecular arrangements with coplanar atoms X, C^α, C^β and C^γ in all cases, e.g. Fig. 3 shows that the γ' signals of the homoadamantenes appear 1.5–2 ppm at lower field than the corresponding γ signals of the adamantanes, although in both cases the torsion angles are equal (180°). This led us to the conclusion that there must be an additional mechanism affecting downfield γ_{anti} SCS.

If we include the two different γ SCS of 1-substituted 2-heteroadamantanes given in Table 2, we find that the γ_C SCS agree with the γ SCS of the corresponding adamantanes rather well, whereas the γ_Y SCS are significantly larger. Similarly, an enhancement of the γ' SCS of bromo-homoadamantene **2d** from 5.3 to 7.5 ppm is observed, if the C-β' methylene group in this molecule is replaced by oxygen to form the corresponding oxa-homoadamantene derivative. This γ' SCS was again obtained by comparison with the corresponding parent compound oxa-homoadamantene.



Scheme 2.

Table 2. ^{13}C γ substituent chemical shifts of 1-substituted 2-heteroadamantanes[a,b]

		X = OH	X = Cl
Y = O	γ_Y:	3.9	6.1
	γ_C:	2.7	3.7
Y = NH	γ_Y:	3.6	4.5
	γ_C:	2.9	3.6
Y = CH_2	γ :	2.3	3.2

[a] Data taken from Ref. 27.

[b] The substituent chemical shifts are given in ppm; positive values correspond to downfield shifts.

Looking at these heteroadamantanes it is found that the shorter the internuclear distances d between the substituents X and the respective γ carbons the larger the downfield increment. Figure 5 shows this graphically.

The distances d are again estimated from Dreiding models, and Fig. 5 can only give a tentative description. Although the d values are only roughly estimated their trend is evident. Furthermore, it should be well noted that the distance d is only a gross parameter depicting a general change in bond lengths and bond angles.

An explanation for the different γ SCS in totally coplanar arrangements may be suggested: Replacing a methylene group by oxygen or a NH group in the adamantane framework the bond lengths and angles are decreased, thus giving smaller d values. By this change of the molecular geometry the hybridization states of the γ_Y carbons are changed slightly causing different γ SCS; in other words, by compressing the molecular moiety in question within the plane like a concertina, the downfield γ SCS can be enhanced remarkably.

For both substituents (X = OH and Cl) the d values of the γ' SCS of the homoadamantenes (● in Fig. 5) do not fit the correlation. This is exactly what we would expect if we consider that there should be a considerable thrust upon the α and the γ' carbons towards each other in the homoadamantene framework (Fig. 6; see also next section).

This should result in a shortening of the parameters d compared with that of the adamantanes. On the other hand, the approach of these two carbons cannot be reproduced by Dreiding models which are too rigid.

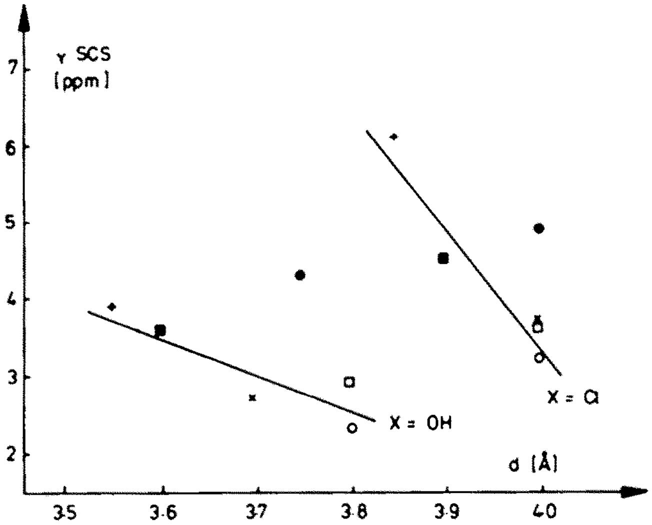


Fig. 5. Substituent effects upon γ positioned carbons (γ SCS) versus the internuclear distances d between the substituents X and the respective γ carbons (●: γ' SCS of **2b** and **2c**; ○: γ SCS of **1b** and **1c**; +: γ_T SCS of the oxaadamantanes; ×: γ_G SCS of the oxaadamantanes; ■: γ_T SCS of the azaadamantanes; □: γ_G SCS of the azaadamantanes).

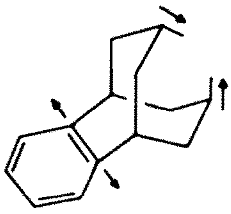


Fig. 6.

To summarize, we obtain from the presented data an insight into the influences of substituents upon γ positioned carbons in bridgehead-substituted molecules. The total γ_{anti} effect is composed of at least two contributions:

$$\gamma\ \mathrm{SCS} = f(\tau, d). \qquad (2)$$

The first parameter describes the angular-dependent downfield γ effect which apparently is operating through the σ bond framework and is only effective, if the torsional angle is relatively large (about 130–180°).

The second parameter represents a mechanism producing changes of γ_{anti} effects by compressing the atomic arrangements X–C$^\alpha$–C$^\beta$–C$^\gamma$ without changing the torsion angle. This effect could only be observed unambiguously for $\tau = 180°$ giving enhancements of the downfield SCS. At the present state of our knowledge it cannot be ascertained whether this term is effective at other torsion angles also, and if it is so, which sign it has.

α-Effect. There are several approaches to interpretation of substituent effects on α carbon shieldings in terms of electronegativity, intramolecular dispersion effects, neighbour-anisotropy effects and others.[7] Although a general concept able to explain these effects on carbons in α position relative to the substituent for a variety of aliphatic compounds does not exist, it is commonly agreed that one major contribution to the αSCS is controlled by the electronegativity of the substituent's atom directly attached to the α carbon.[22]

However, it can be seen clearly from Fig. 7 that electronegativity cannot be the only major contribution. Particularly in the case of the 1-substituted adamantanes **1b–1e** and the homoadamantenes **2b–2e** there is only a very rough correlation between the α effects and the substituents' electronegativities, whereas the corresponding correlation for the homonoradamantenes **3b–3e** is much better.

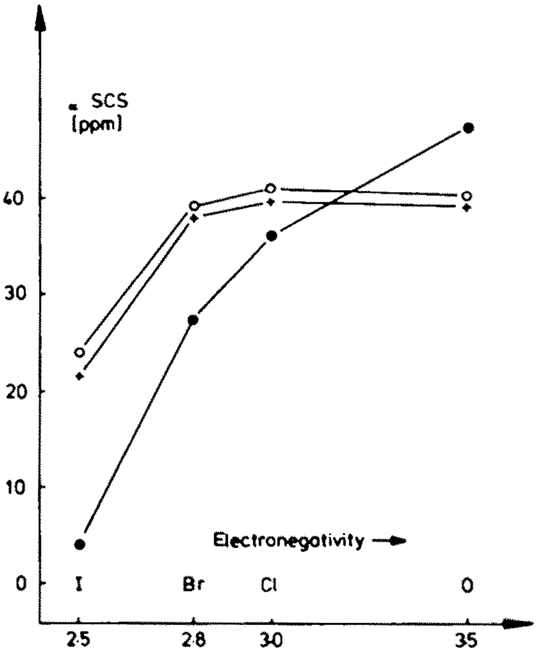


Fig. 7. Substituent effects upon α positioned carbons (α SCS) versus Pauling's electronegativities; +: 1-substituted adamantanes; ○: monosubstituted homoadamantenes; ●: monosubstituted homonoradamantenes.

Grutzner *et al.*[8] established a rule to predict differing α and β effects, as well, by considering the number of substituents other than hydrogen at the α and the β carbons in addition to the inductive effect exerted by the character of the substituent. For hydroxyl and methyl groups they reported a linear correlation between the α shifts and the number n of hydrogens replaced by other substituents at the α and β carbon(s) showing a decrease of the α effects with increasing n in the magnitude of approximately 3 ppm per hydrogen replaced. But already Dorn[21] has pointed out that this concept cannot be generalized to other bicyclic systems and other substituents and that for a given substituent the incremental enhancements of the shielding of the α carbons with increasing n can vary remarkably.

In the present study we calculate n = 5 for the homoadamantenes and n = 6 for the homonoradamantenes. But only for the halogen substituents we found larger α increments for the homoadamantenes than for the homonoradamantenes. For the hydroxy compounds, however, the α SCS is smaller.

Dorn[21] derived from his results that there must be more parameters for explaining the α effects, at least for bicyclic compounds, and suggested taking into account the strain within the molecular framework. He tentatively presented a rough correlation depicting a decay of the α effects with increasing strain estimated from thermodynamic data.[24] But this assumption, if valid at all, cannot be applied to the molecular systems presented in this communication. The three skeletons of the adamantanes, the homoadamantenes and the homonoradamantenes differ significantly in strain.

Whereas the adamantanes can be regarded as nearly free of strain, the widening of one 6-membered ring to a cycloheptene-type ring in the homo- and homonoradamantene series is expected to cause a considerable thrust upon the other bridgehead carbons towards each other (see Fig. 6) which has to be counteracted by the β′ carbon to form the homoadamantenes. To form the homonoradamantenes the approach of the bridgehead carbons has even to be reinforced. Furthermore, in both frameworks the arrangements of the substituents, carbons and hydrogens are distorted from the energetically favoured staggered configurations existing in the adamantane framework, thus causing additional strain due to steric interaction.

Therefore, accepting the tentative model of strain-dependent α SCS one would expect that the α increments of both the homo- and the homonoradamantenes are different from those of the adamantanes for a given substituent. Fig. 7, however clearly demonstrates that at least for the homoadamantenes strain play no larger part affecting the α shifts. They differ from those of the corresponding adamantanes only by +0.6–+2.4 ppm. On the contrary, the α effects of the homonoradamantenes show a completely different behaviour with differences of −17.7 for X = I, −10.3 for X = Br, −3.7 for X = Cl and +7.4 ppm for X = OH.

For that reason we believe that the concept of strain-dependent α SCS cannot be adopted generally, and further investigations are necessary to explain their absolute values and their behaviour within certain series of various substituents in different molecular frameworks.

β Effects. Similar to the α effects the β effects are interpreted in terms of electronegativity and other influences enumerated in the previous section.[7,22] Again one main contribution seems to be the electronegativity, but here the trend is reversed compared with that for the α effects: With increasing electronegativity a decrease of the β increments is observed. This trend is verified by our results.

This sequence has been rationalized by a hypothesis[21,25] suggesting an alternating, decaying charge distribution at the hydrocarbon chain induced by the substituent X:

$$X - C^{\alpha} - C^{\beta} - C^{\gamma} - \cdots$$

$$\delta - \quad \delta + \quad \delta\delta - \quad \delta\delta\delta +$$

Grutzner *et al.*[8] also extended their rule of SCS dependence on the substitution pattern at the α and the β carbons to the β effects and found a steady decay of the β SCS up to n = 3–4. With larger n a constant β SCS is reached. According to this explanation similar values for the β effects in the series **1**, **2** and **3** are expected. Indeed, for a certain substituent all β SCS are the same within a range of 0.7 ppm for the halogens and 1.4 ppm for the hydroxy group.

Long-range effects. All δ SCS of all series and substituents are negative. It is surprising that all δ SCS of halogen substituents are nearly identical (−2.1 ± 0.3 ppm) whatever the molecule and the halogen atom is (chlorine, bromine or iodine). It is even insignificant whether the δ carbon is aliphatic (C-δ of **1** and C-δ′ of **2**) or aromatic (C-δ of **2** and **3**). The hydroxy substituents only differ from the halogen substituents by their absolute values of the δ SCS (−1.5 ± 0.2 ppm), but they show the same behaviour.

The ε effects are very small as they are expected to be (−0.4 to +0.1 ppm), whereas the ζ effects are a little bit larger (0.4–0.7 ppm). Both effects are too small to be interpreted reasonably.

Table 3. ^{13}C chemical shifts (δ) of disubstituted homoadamantenes (series **4**).[a] The values in parentheses are deviations of these experimental values from those calculated by the formula given in the text ($\Delta\delta = \delta - \delta_{calc}$)

	α	β	β′	γ	δ	ε	ζ
4a (= **2a**)	28.8	35.6	36.4	41.6	148.1	128.1	125.9
4c	68.8	43.9	56.0	42.5	144.0	128.3	127.2
	(-6.0)	(0.1)	(-1.4)	(-1.9)	(0.1)	(0.0)	(-0.1)
4d	64.2	44.9	58.2	44.6	143.9	128.2	127.1
	(-9.2)	(0.0)	(-1.8)	(-1.4)	(0.2)	(-0.1)	(0.0)
4e	46.9	47.8	63.4	47.6	144.4	128.2	127.3
	(-11.1)	(0.0)	(-2.4)	(-0.2)	(0.7)	(0.3)	(0.1)

[a] The chemical shifts are relative to tetramethylsilane; positive values correspond to deshielding.

Distributed compounds (*series* 4)

The calculated chemical shifts are obtained with the help of eqn (3):

$$\delta^{k}_{ijk} = A_k + \Delta\delta_i^1 + \Delta\delta_j^2 \qquad (3)$$

with i, j, k = α, β, β', γ, δ, ϵ and ζ.

The A_k are the experimental basic chemical shifts taken from the unsubstituted homoadamantene **2a**, and the $\Delta\delta_i^1$ and $\Delta\delta_j^2$ are the SCS of the two substituents at the α to ζ positioned carbons which have been obtained by comparison of the data of the monosubstituted homoadamantenes **2c**–**2e** and those of homoadamantene **2a** itself (see previous section).

The deviations, $\Delta\delta$, of the experimental and the calculated chemical shifts for the β, β', γ, δ, ϵ and ζ carbons are rather small; only for the β' and the γ carbons small negative discrepancies are observed, i.e. these carbons are slightly more shielded than expected. Only for the α carbons do considerably larger deviations occur which are also negative and increase with increasing atomic weight of the halogen substituents. Similar results were reported very recently by Perkins and Pincock[14] who presented the spectra of 1,3-dihaloadamantanes among other data.

EXPERIMENTAL

The ^{13}C NMR spectra were obtained at natural abundance in the pulsed Fourier transform mode at 22.63 MHz using a Bruker WH-90 spectrometer. The samples were run at a concentration of about 1.5 M in deuterated chloroform with tetramethylsilane as internal standard. Positive values of chemical shifts correspond to downfield shifts. The accuracy of the signals is about ±0.05 ppm.

The compounds **1a** and **1b** are commercially available; the other adamantanes are easily prepared from **1b** by conventional methods. The preparation of the homo- and the homonoradamantenes will be reported in a separate communication.[26]

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