Conformational Effects in β-Functional Acyclic Organosilicon Compounds

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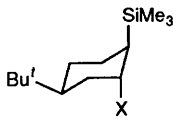
A detailed analysis has been carried out of the proton magnetic resonance (PMR) splitting patterns of the methylene absorptions of β-chloroethyltrimethylsilane at 298 K. The effects of temperature on the PMR spectra of this compound have been examined. In addition, the PMR spectra of β-hydroxyethyltrimethylsilane, β-methoxyethyltrimethylsilane, and β-bromoethyltriphenylsilane were obtained at a number of temperatures. A theoretical analysis of the PMR spectrum of β-chloroethyltrimethylsilane shows that the splitting patterns of the methylene absorptions may be satisfactorily represented by a hindered AA'XX' system of protons. Commercial molecular modelling software has been used to investigate the effects of van der Waals interactions on the conformations of some of these molecules. It is concluded from these various observations that there is severe steric hindrance about the C–C bond of the ethyl moiety in the β-halo systems. For the related β-hydroxy and -methoxy systems the results suggest that the rotation of substituents about the C–C bond is significantly less hindered. These conformational preferences could account for certain steric and kinetic effects observed in such systems.

Recent kinetic studies by Lambert and co-workers[1] have yielded quantitative estimates of the overall β-silicon effect, and the relative magnitudes of the steric and inductive contributions. The rates of solvolysis of the conformationally constrained systems **I** and **II** were measured in trifluoroethanol.

I



II

When X = OCOCF$_3$ it was found that **I** reacted 10^4 times, and **II** 10^{12} times more rapidly than cyclohexyl trifluoroacetate. It was calculated from these results that the antiperiplanar silicon produced an overall stabilisation of the β-carbocation of at least 18 kcal mol^{-1}.† This is considerably less than the value of 38 kcal mol^{-1} predicted by Jorgensen and co-workers[2] for the stabilisation of a cation by a β-silyl group in the gas phase. The difference in the theoretical and the observed values is attributed mainly to the fact that the theoretical value has been derived for the reaction of a primary cation in the gas phase, whereas the observed value refers to the solution reaction of a secondary cation. In the solvent system the nucleophilic solvent will itself provide some stabilisation of the positive charge and this will lessen the demand on the β-silyl system. Using the mathematical expression derived for the calculation of β-secondary deuterium isotope effects it was possible to separate the rate ratios for **I** and **II** into contributions from inductive and hyperconjugative effects. These calculations indicated that the antiperiplanar trimethylsilyl group produced an acceleration of 10^{10} from the hyperconjugative interaction and 10^2 from induction. For the *gauche* geometry the effects were equal; there was an acceleration of 10^2 from both hyperconjugation and induction.

It would appear, from both the theoretical[2] and experimental[1] observations, that steric effects play a major role in determining the high reactivity of β-functional organosilicon compounds. Rates of reaction for systems where the Si group has an antiperiplanar relationship with respect to the leaving group are many orders of magnitude greater than for those systems where there is a *gauche* relationship between the two groups.

It would be expected that the conformationally mobile open chain β-silyl systems $R_3SiCH_2CH_2X$ would exist as a mixture of *gauche* and *anti* forms, and that their overall rate of reaction would depend on the relative concentrations of the two forms and the specific rates at which the individual conformations react.[3]

The PMR spectra of the acyclic β-haloalkylsilanes, $R_3SiCH_2CH_2X$, generally show complex splitting patterns for the $SiCH_2$ and the CH_2X protons and not the simple first-order triplets that would be expected for such systems in which the chemical shift differences are of the order of 2.0–3.0 ppm.[4,5] The oxygenated systems $R_3SiCH_2CH_2OR'$ show splitting patterns much closer to the typical first-order patterns. A possible explanation that has been advanced for the differences in the splitting patterns for the halogen and oxygen substituted compounds is that they arise from differences in conformer distributions in the two systems.

A more detailed analysis of the splitting patterns of several compounds possessing the general structure $R_3SiCH_2CH_2Y$ has been carried out with a view to obtaining additional information on conformational distributions in such systems, and the results are reported here.

Results and Discussion

The proton NMR spectrum of 2-chloroethyltrimethylsilane (**III**) is shown in Fig. 1. The absorptions appear at 1.28 ppm and 3.68 ppm, and correspond to the protons of the silylmethylene and chloromethylene groups respectively. The absoprtions of the methyl groups (*ca.* 0 Hz) are not shown. The spectral details of immediate interest are the splittings of either of the two sets of methylene protons (AA' or XX'); references to XX' from here onwards are arbitrary. From an inspection of the proton NMR spectrum the spin–spin coupling constant for the protons involved in the silylmethylene–chloromethylene interaction is found to be *ca.* 9 Hz, and the difference in their chemical shifts is *ca.* 2.4 ppm (720 Hz). These values would normally be expected to give rise to first-order triplets (*i.e.* a typical, A_2X_2 system). However, at 298 K it is apparent

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† 1 cal = 4.184 J.

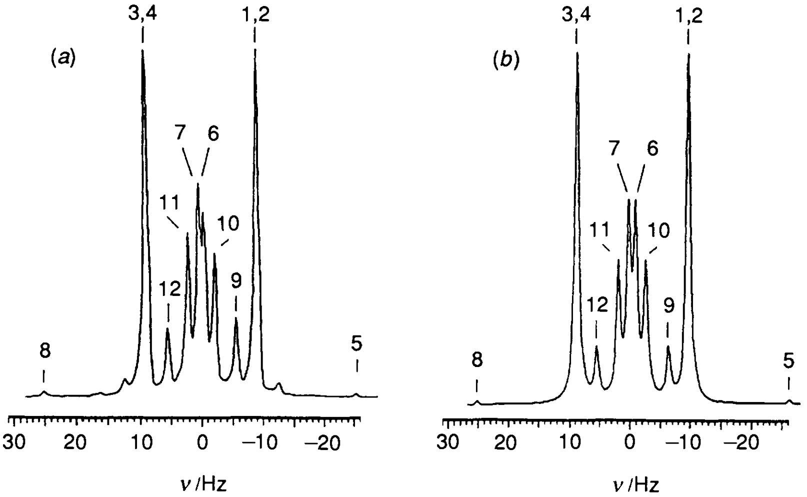

Fig. 1 The experimental (*a*) and theoretical (*b*) proton NMR methylene absorption of 2-chloroethyltrimethylsilane (**III**) at 298 K

Table 1 Positions and relative intensities of lines for the AA′XX′ case[6]

Transition	Position relative to central frequency, ν/Hz[a]	Relative intensity[b]
1	$0.5N$	1
2	$0.5N$	1
3	$-0.5N$	1
4	$-0.5N$	1
5	$0.5[K + (K^2 + L^2)^{1/2}]$	$\sin^2 \theta_s$
6	$-0.5[K - (K^2 + L^2)^{1/2}]$	$\cos^2 \theta_s$
7	$0.5[K - (K^2 + L^2)^{1/2}]$	$\cos^2 \theta_s$
8	$-0.5[K + (K^2 + L^2)^{1/2}]$	$\sin^2 \theta_s$
9	$0.5[M + (M^2 + L^2)^{1/2}]$	$\sin^2 \theta_a$
10	$-0.5[M - (M^2 + L^2)^{1/2}]$	$\cos^2 \theta_a$
11	$0.5[M - (M^2 + L^2)^{1/2}]$	$\cos^2 \theta_a$
12	$-0.5[M + (M^2 + L^2)^{1/2}]$	$\sin^2 \theta_a$

[a] $K = J_{AA'} + J_{XX'}$, $L = J_{AX} - J_{AX'}$, $M = J_{AA'} - J_{XX'}$, $N = J_{AX} + J_{AX'}$.
[b] $\theta_s = 0.5 \cos^{-1}[K/(K^2 + L^2)^{1/2}]$, $\theta_a = 0.5 \cos^{-1}[M/(M^2 + L^2)^{1/2}]$.

that the methylene absorptions differ markedly from first-order triplets.

From a detailed examination of the absorption peaks of the methylene groups it can be seen that each absorption comprises of ten lines. The A and X parts of the spectrum are identical to each other, and each absorption is symmetrical with respect to its central frequency. Fig. 1(*a*) shows an expanded version of the X part (the chloromethylene fragment) of the observed proton NMR spectrum of **III**. For an AA′XX′ system the positions and intensities of the lines in the X (or A) part of the spectrum may be analysed using the relationships listed in Table 1. The lines in the absorption have been labelled according to the entries shown in Table 1. Lines 1, 2, 3 and 4 represent a doublet separated by the quantity *N*. The other lines in the absorption are made up of two quartets. One quartet is associated with the transitions labelled 5, 6, 7 and 8. The remaining quartet is given by transitions 9, 10, 11 and 12. It is clear from a comparison of the entries in Table 1 and the spectrum in Fig. 1(*a*) that all of the possible NMR transitions can be seen for this compound. The magnitudes of the parameters *K*, *M* and *N* can be readily deduced by direct measurement of line spacings in either the X or A absorptions, following the procedure given by Wiberg and Nist.[6] Thus, for **III**, the parameters *K*, *M* and *N* were found to be 24.4 Hz, 3.5 Hz and 17.9 Hz respectively. The difference between lines 5 and 7 [Fig. 1(*a*)] gives $(K^2 + L^2)^{1/2}$, which may be used to obtain the modulus of *L*. The time-averaged values of the coupling constants were then deduced to be $J_{AA'}$ = 14 Hz, $J_{XX'}$ = 10.5 Hz, J_{AX} = 12.5 Hz and $J_{AX'}$ = 5.4 Hz. The signs of the coupling constants have been assumed to be positive since it is not possible to derive the absolute signs of the coupling constants using this type of analysis. Fig. 1(*b*) shows the theoretical absorption of the XX′ (or AA′) part of the AA′XX′ interaction, calculated using the coupling constants obtained from the analysis of the observed absorption peak. Comparison of the experimental (*a*) and theoretical (*b*) absorptions, shown in Fig. 1, indicates a close match with respect to line positions and intensities. The application of a simple $\cos^2 \theta$ Karplus relationship enables an estimate to be made of the rotamer population of **III**. From the coupling data derived in the proceding sections it is concluded that at 298 K **III** exists predominantly (73%) in the *anti* form. This corresponds to a difference in energy between the *anti* and *gauche* rotamers of close to 1 kcal mol^{-1} (4.2 kJ mol^{-1}). The small lines positioned slightly upfield and downfield of the N transition arise from couplings with the silicon atom (natural abundance *ca.* 5%). In addition, dipole moment measurements[7] and an examination of van der Waals interactions using a molecular modelling computer program[8] (see below) both indicate that, at room temperature, **III** exists predominantly in the *anti* conformation. We note that the figure of 73% obtained for the population of the *anti* form is subject to uncertainties arising from the effects of substituent electronegativities, which were not included in these calculations.

The spectra of **III** obtained at higher temperatures more closely resemble first-order triplets (Fig. 2). Raising the temperature increases the population of *gauche* rotamers and the high temperature limiting condition $J_{AX} = J_{AX'}$ = *ca.* 9 Hz is more closely approached. The spectral changes induced by changes in temperature were found to be entirely reversible [*c.f.* Fig. 2(*a*) and (*f*)]. At the maximum achieved temperature of 408 K the time-averaged coupling constant was estimated to be 11.7 Hz, which corresponds to 63% of the *anti* rotamer.

It is interesting to compare the proton NMR spectra for various types of β-functional alkylsilanes. Fig. 3 shows the AA′ and the XX′ parts of the ^{1}H spectrum at 298 K for a series of alkylsilanes having the general structure $R_3SiCH_2CH_2Y$. It is noted that the methylene and methyl absorptions of ethyltrimethylsilane (spectrum not included) closely resemble a quartet and a triplet, respectively, but are significantly asymmetric in shape because of second-order effects. For the more highly substituted 2-bromoethyltriphenylsilane (**IV**) the methylene absorptions were complex and remained almost unchanged over the whole range of accessible temperatures (298–408 K). It would appear that for this compound there is considerable steric hindrance between the triphenylsilyl group

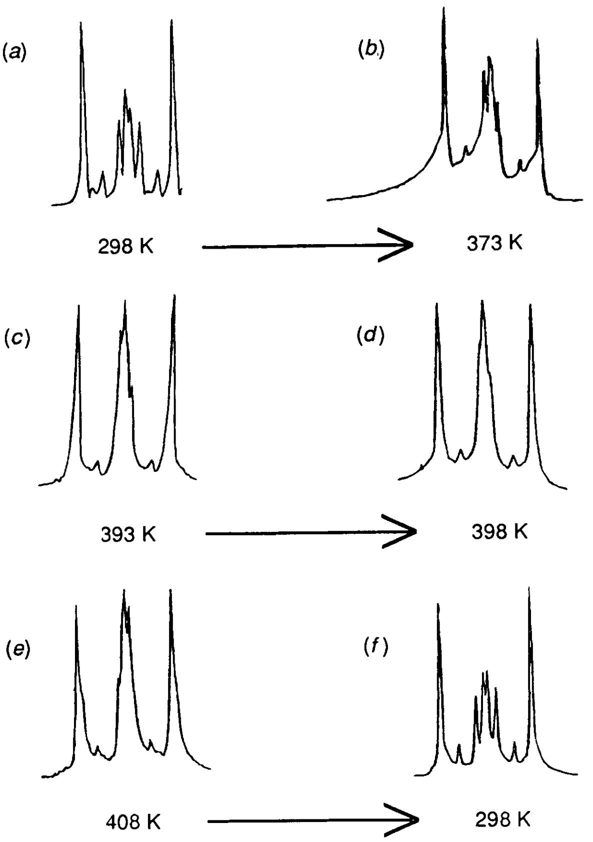

Fig. 2 The proton NMR methylene absorption of 2-chloroethyltrimethylsilane (**III**) at various temperatures

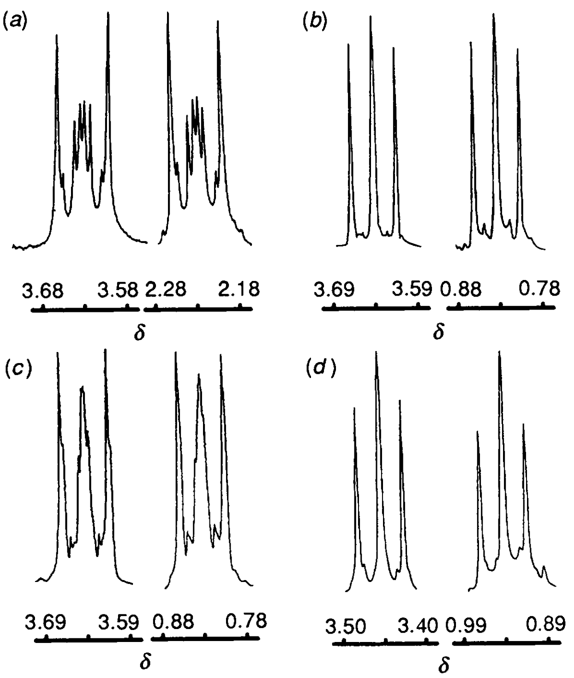

Fig. 3 Proton NMR methylene absorptions of 2-bromoethyltriphenylsilane in deuteriated dimethyl sulfoxide (*a*), 2-hydroxyethyltrimethylsilane in *p*-xylene (*b*), 2-hydroxyethyltrimethylsilane in $CDCl_3$ (*c*) and 2-methoxyethyltrimethylsilane in *p*-xylene (*d*) at 298 K

and the bromo substituent of the ethyl moiety, and that, as a consequence, this molecule exists almost entirely in the *anti* form up to the maximum observed temperature of 408 K. However, although the 2-bromoethyltriphenylsilane is held rigidly in the preferred conformation for elimination, it does not react solvolytically.[9] It was originally reported by Sommer[10] that electronegative substituents at silicon retard the elimination reaction; $C_6H_5(CH_3)_2SiCH_2CH_2Cl$ reacts more rapidly than $m\text{-}CF_3C_6H_4(CH_3)_2SiCH_2CH_2Cl$. If there are electronegative substituents at silicon it seems that electronic effects may become more important than steric factors in determining reactivity.

The methylene absorptions of the 2-hydroxyethyltrimethylsilane **V** [Fig. 3(*b*)] and 2-methoxyethyltrimethylsilane **VI** [Fig. 3(*d*)] more closely resemble first-order triplets, and these spectra did not show any significant changes as the temperature was increased. It is of interest that the PMR spectrum of 2-hydroxyethyltrimethylsilane measured in solution in chloroform [Fig. 3(*c*)] departs significantly from the triplet-like spectrum observed for this compound when dissolved in *p*-xylene. A possible, simple explanation of these observations is that there is hydrogen bonding between the solute and the solvent, which effectively increases the size of the hydroxy substituent, and further stabilises the *anti* conformer. It is also possible that the coupling constants may be influenced by the solvent.

A commercial molecular modelling program[8] was used to evaluate the relative effects resulting from differences in the van der Waals radii of chlorine and oxygen on the conformations of **III**, **V** and **VI**. Fig. 4 shows the *anti*, eclipsed (with respect to silyl and β substituents) and *gauche* conformations of **III**, **V** and **VI**. In all cases the eclipsed form is sufficiently high in energy, relative to the other rotamers, that its statistical weighting can be regarded as zero. It is apparent from even a visual examination of the conformations shown in Fig. 4 that there is an appreciably greater interaction between the chlorine atom and the trimethylsilyl group [Fig. 4(*c*)] than that between the smaller oxygen and the trimethylsilyl group [Fig. 4(*a*) and (*b*). The van der Waals covalent radii (and van der Waals volumes, v) for chlorine and oxygen are 0.140 nm (v = 0.115 nm^3) and 0.180 nm (v = 0.244 nm^3), respectively,[11] which could explain why the hydroxy and methoxy groups appear to cause significantly less steric hindrance than the chlorine atom. For **III** the molecular modelling program indicated that the *gauche* rotamers are not located at ± 120° relative to the *anti* rotamer (defined as 0°) but are displaced to about ± 100°. If it is assumed that the *gauche* forms have dihedral angles of about ± 100° then the simple $\cos^2 \theta$ Karplus equation would predict that the *anti* rotamer population of **III** is increased from 73% to 79% at 298 K and from 63% to 69% at 408 K.

Although the observation of triplets for the methylene absorptions of the β-hydroxy and β-methoxy compounds indicates relatively equal statistical weightings of *anti* and *gauche* rotamers it is noted that the 'accidental' equivalence of the J_{AX} and $J_{AX'}$ coupling constants would give rise to symmetrical triplet methylene absorptions, even for molecules that possessed a dominance of either the *anti* or *gauche* rotamer forms. The general effects on the AA' (or XX') parts of the proton NMR methylene absorptions, brought about by varying the relative values of J_{AX} and $J_{AX'}$, are shown in Fig. 5. It is useful to compare the absorptions shown in this figure with the experimental absorptions of **IV**–**VI** presented in Fig. 3.

It would appear that for the β-functional oxygenated systems the *anti* and *gauche* rotamers for the 2-substituted ethyltrimethylsilyl systems are approximately equally weighted, but that as the size of the substituents on silicon increases, the rotation about the C–C bond becomes more restricted and the favoured rotamer is the *anti* form.

These conformational effects provide one possible explanation for the dependence of the relative rates of solvolysis of the β-hydroxy and β-halo systems on the size of the substituents. In earlier studies Sommer[10] observed that for β-hydroxy com-

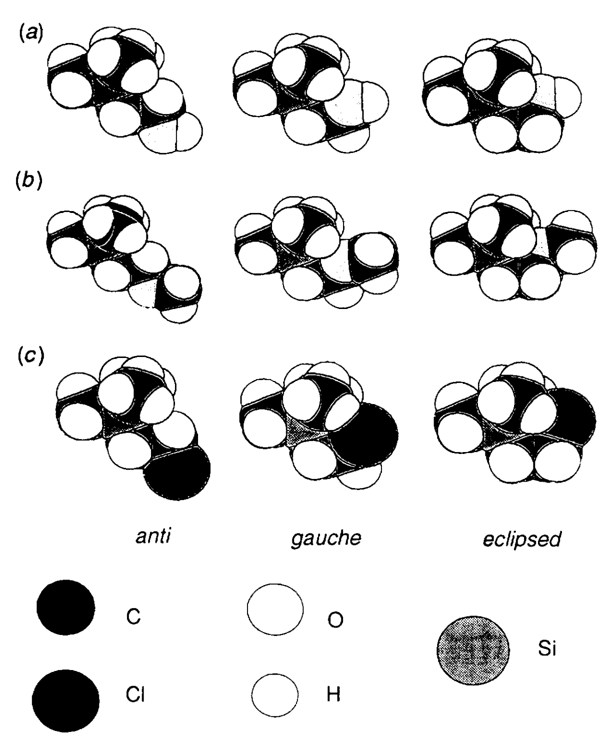

Fig. 4 Van der Waals scale models showing the *anti*, *gauche* and eclipsed conformations of (*a*) 2-hydroxyethyltrimethylsilane, **V**; (*b*) 2-methoxyethyltrimethylsilane, **VI**; and (*c*) 2-chloroethyltrimethylsilane, **III**

pounds the solvolysis rate increased in the order Me$_3$Si < EtMe$_2$Si < Et$_2$MeSi < Et$_3$Si. It may be that, in the case of the hydroxy systems, as the size of the substituent is increased the population of the *anti* conformation, the preferred conformation for elimination, also increases. In contrast, for the β-chloroethyl systems the solvolysis rate is very similar to the Me$_3$Si and Et$_2$MeSi compounds. Since in the Me$_3$Si system the dominant conformer is the *anti* form, a further increase in the size of the substituents has little effect on the rate of solvolysis. The observations of Sommer[10] are fragmented and not entirely consistent. They are, however, the only comparative studies of the effects of substituent size on the reactivity of the β-chloro and β-hydroxy systems. There are obviously other possible explanations for the effect of substituent size on the reactivity of these systems, and more detailed comparative studies would have to be carried out to evaluate the relative importance of such effects.

High stereospecificity in addition and elimination reactions is a common characteristic of R$_3$SiCC systems.[12] The stereospecific bromination and deuteriation of (*Z*)- and (*E*)-β-trimethylsilylstyrene was observed by Koenig and Weber,[13] who rationalised their observations by assuming that, simultaneously with addition of the electrophile to the double bond, rotation occurs about the developing C–C single bond in such a direction as to permit the C–Si bond to stabilise continuously the incipient benzylic carbonium ion. Colvin[12] has pointed out that this retention of alkene geometry is quite general, and is not restricted to silylstyrenes.

It would appear that for silanes of the type R$_3$SiCH$_2$CH$_2$Y the *anti* rotamer is dominant at room temperature, unless R and Y (especially) are small.

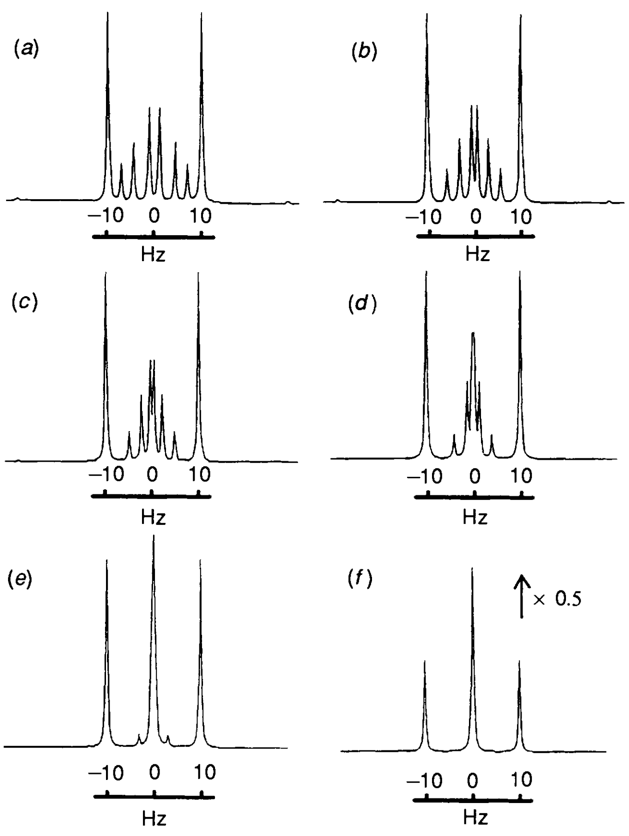

Fig. 5 Theoretical proton NMR spectrum of the AA′XX′ system showing the AA′ (or XX′ absorption): (*a*) J_{AX} = 14 Hz, $J_{AX'}$ = 4 Hz (94%); (*b*) J_{AX} = 13 Hz, $J_{AX'}$ = 5 Hz (80%); (*c*) J_{AX} = 12 Hz, $J_{AX'}$ = 6 Hz (67%); (*d*) J_{AX} = 11 Hz, $J_{AX'}$ = 7 Hz (55%); (*e*) J_{AX} = 10 Hz, $J_{AX'}$ = 8 Hz (44%); (*f*) J_{AX} = 9 Hz, $J_{AX'}$ = 9 Hz (33%). In all cases $J_{AA'}$ = 14 Hz and $J_{XX'}$ = 11 Hz. The figure in brackets is the calculated amount of the *anti* rotamer, calculated using ΔH (*gauche*) = 4.2 kJ mol^{-1} (energy of *anti* rotamer defined as zero).

Experimental

Spectra.—^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC300 MHz spectrometer (solutions in CDCl$_3$ unless otherwise stated). The ^{13}C spectra were obtained using the APT (JMOD) pulse sequence with a digital resolution of 1.09 Hz per point and an acquisition time of 0.92 s. The temperature studies were carried out in deuteriated xylene([^{2}H$_{10}$]-*p*-xylene, Aldrich).

Computational.—Molecular modelling calculations were performed on a 66 MHz, IBM 486 compatible computer using commercial computer software.[8] The theoretical spectra were calculated using a computer program written in Microsoft QBASIC using the entries listed in Table 1.

Materials.—2-Chloroethyltrimethylsilane [(61%), b.p. 39 °C/2 mmHg; δ_H −0.03 (s, 9 H), 1.15 (m, 2 H), 3.66 (m, 2 H); δ_C −1.78, 20.7, 43.2]; 2-hydroxyethyltrimethylsilane [(77%), b.p. 52 °C/2 mmHg; δ_H −0.31 (s, 9 H), 0.83 (m, 2 H), 3.64 (m, 2 H), 3.78 (s, 1 H); δ_C −2.09, 22.9, 58.4]; 2-methoxyethyltrimethylsilane [(30%) b.p. 38 °C/0.6 mmHg; δ_H −0.06 (s, 9 H), 0.94 (m, 2 H), 3.22 (s, 3 H), 3.45 (m, 2 H); δ_C 0.35, 26.0, 64.4], were all prepared by the method of Wilt and co-workers[14] (spectra were in agreement with those reported). 2-Bromoethyltriphenylsilane was prepared according to the method of Sommer and co-workers[15] (88%), m.p. 90 °C; δ_H 2.23 (m, 2 H), 3.63 (m, 2 H), 7.52 (m, 15 H).

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