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CLXXXIII *. AN ESR STUDY ON β-TRIMETHYLSILYLAMINE- AND RELATED AMINE-*N*-OXYLS. UNUSUAL CONFORMATIONAL PREFERENCE OF THE β-SILYL GROUP

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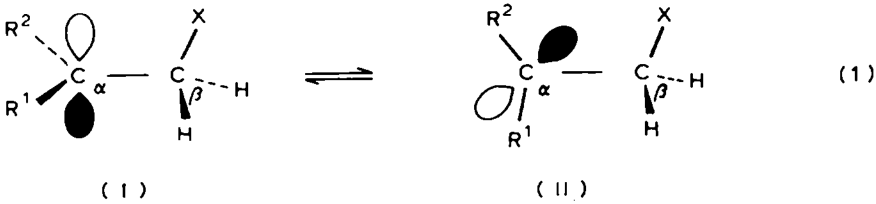
Summary

Fifteen β-trimethylsilylamine- and related amine-*N*-oxyls were generated by oxidation of the parent amines with *m*-chloroperoxybenzoic acid. Studies on the preferred conformation of the radicals by ESR spectroscopy indicate that the β-trimethylsilyl group exerts a strong influence favouring the conformation in which the trimethylsilyl group lies in the same plane as the N–O bond. The ESR spectra of related alkyl radicals, as well as results of unrestricted CNDO/2 calculations on the silylmethylamine-*N*-oxyls, are discussed.

Introduction

The conformational preferences of β-substituted ethyl radicals of the type $XCH_2\dot{C}R^1R^2$ have been extensively investigated by ESR spectroscopy [1,2]. As far as we know, all the studies on Group IVB metal-substituted ethyl and related radicals have indicated that the preferred conformation at low temperatures is I, in which X ($= SiR_3$, GeR_3, and SnR_3) eclipses the singly occupied *p*-orbital (SOMO) (Scheme 1). This conformational preference has been reasonably explained in terms of



SCHEME 1

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[*] For Part CLXXXII see ref. 19.

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enhanced σ–π conjugation between the SOMO and a C–M σ-bonding orbital and/or p–d homo-conjugation where vacant d-orbitals of a metal atom are used. Although both interactions can be important in determining the preferred conformation, they may be rather weak because either two-bond three-electron or one-electron interaction is involved. As a consequence, the conformational equilibrium of these radicals may be affected easily by other types of electronic interaction such as steric repulsion, non-bonding attraction, solvation, and so on.

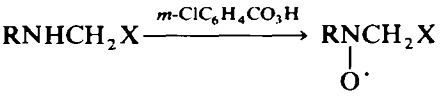
We wish to report that β-organometalloid-substituted amine-*N*-oxyl radicals have a remarkably different conformational preference to that of the corresponding β-trialkylsilyl-substituted alkyl radicals, as determined by the β-proton hyperfine splitting constants (hfsc) in their ESR spectra. In the former radicals, the position of the conformational equilibrium was such that both I and II were present, indicative of the importance of other types of interaction which function in the opposite direction to the σ–π and/or homo $(p$–$d)\pi$ conjugations. It is noted also that the conformational preference of the amine-*N*-oxyls depends on the solvent polarity. Non-bonding attraction between the silyl and the N–O groups involving Si d (or σ^*)-orbital participation is investigated as an important factor in controlling such rather unusual conformational preferences.

Results and discussion

Generation and ESR spectra of amine-N-oxyls

Although there have been extensive studies on the conformational problems of amine-*N*-oxyls [3,4a], no systematic study on the preferred conformation of β-Group IVB-metal-substituted amine *N*-oxyls has appeared to date. A variety of alkyl- and aryl-amine-*N*-oxyls have been generated conveniently by the oxidation of appropriate secondary amines with *m*-chloroperoxybenzoic acid in various solvents (eq. 2) [3].

Although some alkyl(trimethylsilylmethyl)amine-*N*-oxyls gave ESR signals which were too weak for the ESR parameters to be obtained in solvents such as hydrocarbons, alcohols, and carbon tetrachloride, most of the amine-*N*-oxyls investigated here yielded well-resolved ESR spectra in a variety of solvents. Representative examples are shown in Figs. 1–5. The derived ESR parameters are compiled in



$$RNHCH_2X \xrightarrow{m\text{-}ClC_6H_4CO_3H} R\underset{\underset{\displaystyle O^{\bullet}}{|}}{N}CH_2X \qquad (2)$$

(**1a** R = CH_3 X = H
1b R = X = CH_3
1c R = CH_3, X = $SiMe_3$
1d R = CH_3, X = $GeMe_3$
2b R = Et, X = CH_3,
2c R = Et, X = $SiMe_3$
3a R = t-Bu, X = H,
3b R = t-Bu, X = CH_3
3c R = t-Bu, X = $SiMe_3$
4c R = CH_2SiMe_3, X = $SiMe_3$
5c R = CH_2SiMe_2Ph, X = $SiMe_2Ph$
6a R = Ph, X = H
6b R = Ph, X = CH_3
6c R = Ph, X = $SiMe_3$
6d R = Ph, X = $SiMe_2Ph$)

(Continued on p. 55)

Fig. 1. (a) ESR spectrum of methyl(trimethylsilylmethyl)amine-*N*-oxyl (**1c**) in benzene at room temperature; (b) simulated spectrum.

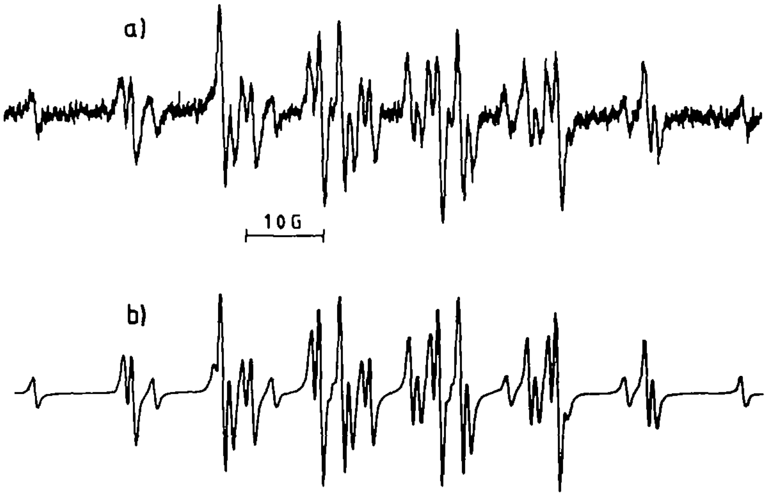


Fig. 2. (a) ESR spectrum of methyl(trimethylgermylmethyl)amine-*N*-oxyl (**1d**) in benzene at room temperature; (b) simulated spectrum.

Fig. 3. ESR spectrum of bis(trimethylsilylmethyl)amine-*N*-oxyl (**4c**) in benzene at room temperature.

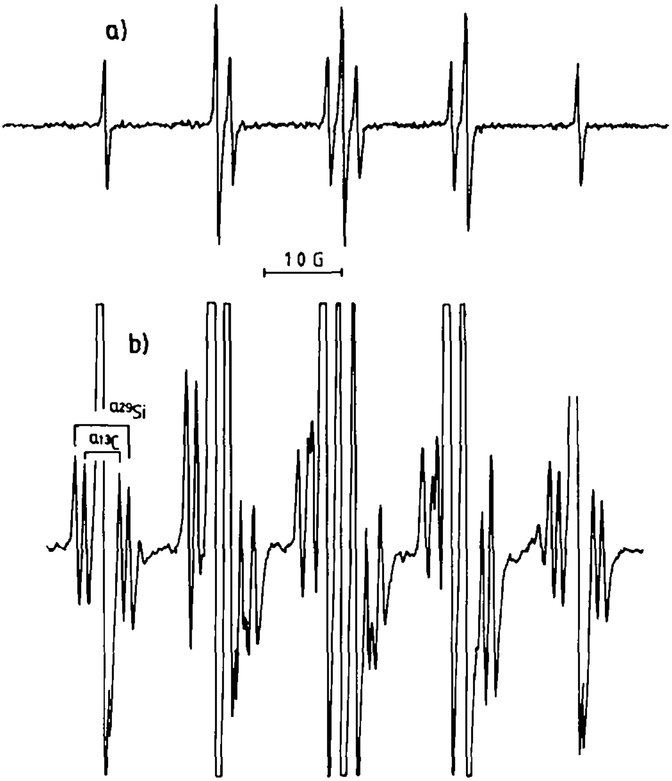


Fig. 4. (a) ESR spectrum of t-butyl(trimethylsilylmethyl)amine-*N*-oxyl (**3c**) in $CHCl_3$ at room temperature; (b) Two satellite spectra attributed to those with 5.5% of ^{13}C and 4.7% of ^{29}Si.

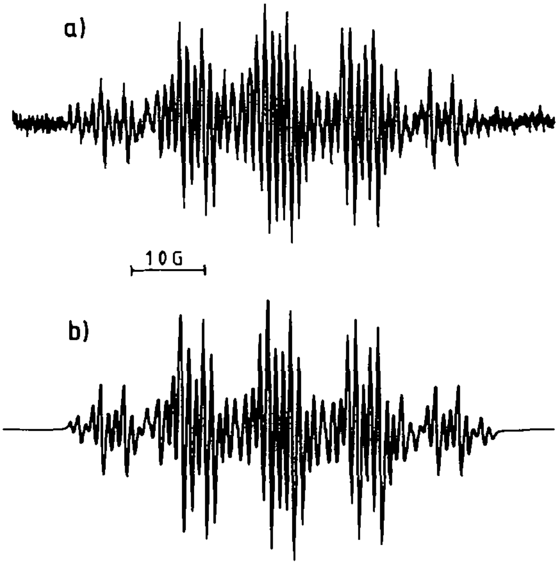


Fig. 5. (a) ESR spectrum of phenyl(trimethylsilylmethyl)amine-*N*-oxyl (**6c**) in $CHCl_3$ at room temperature; (b) simulated spectrum.

Tables 1–3. t-Butyl(trimethylsilylmethyl)amine-*N*-oxyl (**3c**) was produced in a rather high concentration in chloroform and dichloromethane so as to allow observation of satellite spectra assigned to a mixture of two species containing γ-^{13}C and ^{29}Si nuclei. Phenylamine-*N*-oxyls were relatively long-lived in a wide variety of solvents, thus allowing the investigation of solvent effects on the conformational preference.

Structurally similar α-substituted β-trimethylsilylethyl radicals, obtained in the di-t-butyl peroxide initiated addition of trimethylsilyl radicals to the appropriate olefins (eq. 3) [1a], were also investigated by ESR. The ESR parameters are listed in Table 4, together with some other pertinent data.

$$\begin{array}{lll} Me_3SiH & + \text{t-BuO}^{\cdot} & \rightarrow \; Me_3Si^{\cdot} + \text{t-BuOH} \\ Me_3Si^{\cdot} & + R\text{–}CH{=}CH_2 & \rightarrow \; R\text{–}\dot{C}HCH_2SiMe_3 \\ & & \quad (\mathbf{7}\; R = CH_3, \\ & & \quad\; \mathbf{8}\; R = C(CH_3)_3, \\ & & \quad\; \mathbf{9}\; R = CH_2SiMe_3) \end{array} \qquad (3)$$

Conformational analysis

The problem as to whether the configuration around the nitrogen atom of

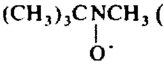
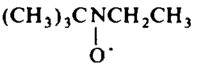
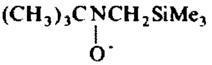
TABLE 1

HYPERFINE SPLITTING CONSTANTS OF β-SUBSTITUTED DIMETHYLAMINE-*N*-OXYLS AT AMBIENT TEMPERATURE

Radical	Solvent	a^N (G)	$a^H_{\beta\text{-CH}_2}$ (G)	$a^H_{\beta\text{-CH}_3}$ (G)
$CH_3\underset{O^{\cdot}}{\underset{\mid}{N}}CH_3$ (**1a**)	CCl_4	15.1	–	12.4
	C_6H_6	15.2	–	12.4
$CH_3\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2CH_3$ (**1b**)	CCl_4	15.2	10.4	12.3
	C_6H_6	15.2	10.3	12.4
	CH_2Cl_2	15.7	10.7	12.7
$CH_3\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2SiMe_3$ (**1c**)	C_6H_6	15.4	12.7	12.7
	CH_2Cl_2	15.7	12.1	13.1
$CH_3\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2GeMe_3$ (**1d**)	C_6H_6	15.2	11.5	12.5
$CH_3CH_2\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2CH_3$ (**2b**)	CCl_4	15.1	10.5	–
$CH_3CH_2\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2SiMe_3$ (**2c**)	C_6H_6	15.4	10.7 13.2	–
$Me_3SiCH_2\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2SiMe_3$ (**4c**)	CCl_4	15.4	13.5	–
	$CHCl_3$	15.9	12.8	–
$PhMe_2SiCH_2\underset{O^{\cdot}}{\underset{\mid}{N}}CH_2SiMe_2Ph$ (**5c**)	CCl_4	15.4	13.4	–
	$CHCl_3$	15.8	12.3	–

TABLE 2

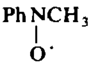
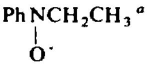
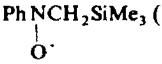
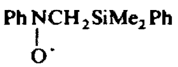
HYPERFINE SPLITTING CONSTANTS[a] OF β-SUBSTITUTED METHYL-t-BUTYLAMINE-*N*-OXYLS AT AMBIENT TEMPERATURE

Radical	Solvent	a^N (G)	$a^H_{\beta\text{-}CH_2}$ (G)	$a(^{29}Si)$ (G)	$a(^{13}C)$ (G)
 $(CH_3)_3C\underset{O^{\cdot}}{\underset{\vert}{N}}CH_3$ **(3a)**	CCl_4	15.8	11.7	–	4.9
 $(CH_3)_3C\underset{O^{\cdot}}{\underset{\vert}{N}}CH_2CH_3$ **(3b)**	CCl_4	15.2	10.3	–	4.9
	CH_2Cl_2	15.7	10.4	–	–
 $(CH_3)_3C\underset{O^{\cdot}}{\underset{\vert}{N}}CH_2SiMe_3$ **(3c)**	CCl_4	15.9	14.5	–	–
	$CHCl_3$	16.3	14.4	6.8	4.6
	CH_2Cl_2	16.4	14.4	7.0	4.8
	CH_3OH	16.5	14.5	–	–

[a] The ^{13}C hfsc's were assigned to 3 methyl carbons on the t-butyl group and 2 carbons of N–C bonds having incidentally equal hfsc's.

TABLE 3

HYPERFINE SPLITTING CONSTANTS OF *N*-ALKYLANILINE-*N*-OXYLS AT AMBIENT TEMPERATURE

Radical	Solvent	Hfsc (G)			
		N	β-CH_2	*o,p*-H	*m*-H
 $Ph\underset{O^{\cdot}}{\underset{\vert}{N}}CH_3$ **(6a)**	CCl_4	10.9	10.0	2.8_6	0.9_6
	Et_2O	10.5	9.7	2.8_0	0.8_6
	C_6H_6	11.0	10.4	2.7_7	0.9_6
	$CHCl_3$	11.2	10.3	2.9_2	1.0_1
	CH_2Cl_2	11.1	10.3	2.8_5	0.9_5
	CH_3CN	11.1	10.2	2.9_4	1.0_0
	CH_3OH	11.6	10.6	2.9_5	0.9_8
 $Ph\underset{O^{\cdot}}{\underset{\vert}{N}}CH_2CH_3$[a] **(6b)**	CCl_4	10.6	7.8_5	2.8_6	0.9_6
	Et_2O	10.5	7.8_1	2.7_6	1.0_0
	C_6H_6	10.7	7.9_3	2.7_7	0.9_4
	$CHCl_3$	11.2	7.8_2	2.9_8	1.0_0
	CH_3CN	10.9	7.9_9	2.9_9	1.0_0
	CH_3OH	11.6	7.8_4	3.0_0	0.9_6
 $Ph\underset{O^{\cdot}}{\underset{\vert}{N}}CH_2SiMe_3$ **(6c)**	CCl_4	10.6	10.8	2.8_2	1.1_0
	Et_2O	10.6	10.9	2.8_4	1.0_0
	C_6H_6	10.7	10.7	2.8_6	0.9_9
	$CHCl_3$	11.3	10.2	2.9_3	1.0_0
	CH_2Cl_2	11.2	10.1	2.8_8	1.0_0
	CH_3CN	11.1	10.2	2.9_9	0.9_7
	CH_3OH	11.8	9.9_9	3.0_3	1.0_0
 $Ph\underset{O^{\cdot}}{\underset{\vert}{N}}CH_2SiMe_2Ph$ **(6d)**	CCl_4	10.8	11.0	2.8_3	1.0_0
	$CHCl_3$	11.3	10.5	2.9_0	1.0_0
	CH_3OH	11.6	10.1	3.0_0	1.0_0

[a] γ-H hyperfine splittings were not resolved.

TABLE 4

HYPERFINE SPLITTING CONSTANTS OF SOME ALKYL RADICALS AT LOW TEMPERATURE

Radical	Temp (°C)	Hfsc (G)			
		α-H	β-CH_2	β-CH_3	Others
$(CH_3)_3C\dot{C}HCH_2SiMe_3$ [a]	−101	21.5	21.5		0.6 (γ-H)
$(CH_3CH_2)_3C\dot{C}HCH_3$ [b]	−30	21.7	24.9		
$(Me_3SiCH_2)_2\dot{C}H$ [a]	−53	20.3	17.3		
$(CH_3)_2\dot{C}H$ [b]	−85	22.11		24.68	
$CH_3\dot{C}HCH_2CH_3$ [c]	−60	22.0	26.75	24.8	
$CH_3\dot{C}HCH_2SiMe_3$ [a]	−60	21.2	17.2	24.3	

[a] Present work. These radicals were generated as described in the text. [b] R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 39 (1963) 2147. [c] Present work. This radical was generated by the photolysis of the mixture of s-butyl bromide, trimethylsilane and di-t-butyl peroxide.

dialkylamine-*N*-oxyls is pyramidal or planar is very interesting and is the subject of extensive discussion [4]. However, the planar configuration was assumed here for all the investigated dialkylamine-*N*-oxyls (a_N = 15.1–16.5 G) as well as for *N*-alkylaniline-*N*-oxyls (a_N = 10.5–11.8 G) because of these rather small a_N values.

One point of interest in the conformational information is the angular dependence of the β-proton coupling constants. The time-averaged $a^{H}_{\beta\text{-}H}$ can be described by the McConnell-Heller's equation [4a,5] (eq. 4),

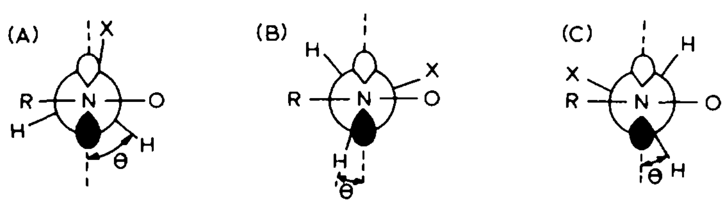
$$a^{H}_{\beta\text{-}H} = \rho_N\left(B_0 + B\langle\cos^2\theta\rangle\right) \tag{4}$$

where ρ_N is the spin density on nitrogen, θ is the dihedral angle between the N–C–H plane and the axis of the p_z orbital of the *N*-oxyl nitrogen atom. Assuming the independence of ρ_N on the β-substituents and that $B_0 \simeq 0$ (eq. 5), the ratio of hfsc's of the β-proton to the methyl-proton in question [6] should be approximately equal to $2\langle\cos^2\theta\rangle$, the time-averaged value of $2\cos^2\theta$. The former assumption is supported

$$R \equiv a^{H}_{\beta\text{-}CH_2}/a^{H}_{\beta\text{-}CH_3} \simeq 2\langle\cos^2\theta\rangle \tag{5}$$

by the similar a^N values observed among the series: $RN(\dot{O})CH_3$, $RN(\dot{O})CH_2CH_3$, and $RN(\dot{O})CH_2SiMe_3$, with the same R group.

In amine-*N*-oxyls, $RN(\dot{O})CH_2X$, the three different limiting conformations shown in Scheme 2 should be considered. For steric reasons, conformation C can be excluded, especially in the presence of a bulky substituent R [3c]. Most dialkylamine-*N*-oxyls (X = alkyl) generally favour the conformation A, although the actual structure may be a less symmetrical one because of the different steric requirements of R and O [4a]. In addition to above observation, σ–π and homo(p–d)π conjugations are expected to make the conformation A more favourable, and as a result R values smaller than unity may be expected for these β-Group IVB-metal substituted alkylamine-*N*-oxyls. The experimental results show some rather unusual aspects, however.



SCHEME 2

First, let us compare the *R* values of the methylamine-*N*-oxyls **1a–1d** in benzene with those of the corresponding carbinyl radicals, $CH_3\dot{C}HCH_2X$ (X = H, CH_3, and $SiMe_3$; see Table 5). Since the methyl and the substituted-methyl groups are bound to the same radical center in each series of radicals, the *R* values in the averaged conformation can be estimated straightforwardly by using eq. 5.

The *R* values, with benzene as the solvent are listed in Table 5. Strikingly, the *R* value of **1c** was observed to be unity, i.e., it has the same $a^{H}_{\beta\text{-CH}_2}$ value as that for the freely rotating methyl group, while the corresponding carbinyl radical showed a small *R* value of 0.71 which is reasonably to be expected from the preferred conformation of $^{\cdot}CH_2CH_2SiR_3$ found in previous studies. The unusual conformational preference found for trialkylsilylmethylamine-*N*-oxyls can be seen to be rather general, when the $a^{H}_{\beta\text{-CH}_2}$ values for **2b**, **2c**, **3a–3c**, and **6a–6d** are compared. Thus, it can be suggested that in organosilylmethylamine-*N*-oxyls an interaction favouring the conformation B exists to counterbalance the driving force in favour of the conformation A, such as σ–π conjugation and $(p\text{–}d)\pi$ homo-conjugation.

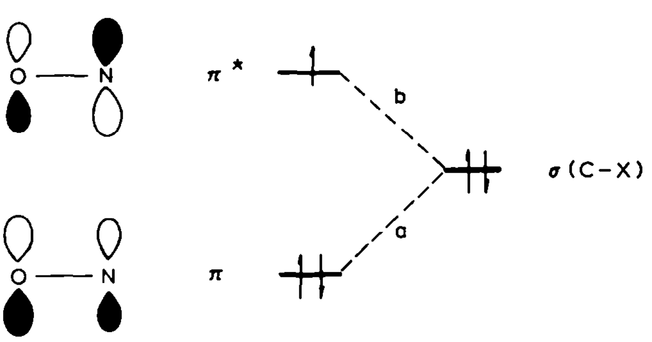
Two important interaction models may be considered to account for such an anomalous conformational preference, as follows:

(a) It has recently been proposed, on the basis of perturbation MO theory, that for substituted carbonium ions, $\overset{+}{C}H_2CH_2X$, the conformation I in Scheme 1 is favoured (whereas II is taken by the corresponding carbanions), due to hyperconjugation when X is more electropositive than H [7]. Three electrons of an N–O bond reside in π and π^* orbitals derived from the linear combination of the nitrogen and oxygen $p\pi$ orbitals, as shown in Scheme 3. The destabilizing interaction "a" may be more important than the weak stabilizing three-electron two-orbital interaction "b", leading to the favoured conformation B in Scheme 2, where the interaction "a" could be avoided. Since the destabilizing interaction of two filled orbitals does not depend on the energy separating the two interacting MO's, but rather on the average of their energies [8], electropositive substituents, X, may cause larger destabilization

TABLE 5

R VALUES OF β-SUBSTITUTED DIMETHYLAMINE-*N*-OXYLS ($CH_3N(\dot{O})CH_2X$) AND β-SUBSTITUTED ISOPROPYL RADICALS ($CH_3\dot{C}HCH_2X$) IN BENZENE

X	*R*-value	
	$CH_3N(\dot{O})CH_2X$	$CH_3\dot{C}HCH_2X$
H	*1.00*	*1.00*
CH_3	0.83	1.09
$SiMe_3$	1.00	0.71
$GeMe_3$	0.92	–



SCHEME 3

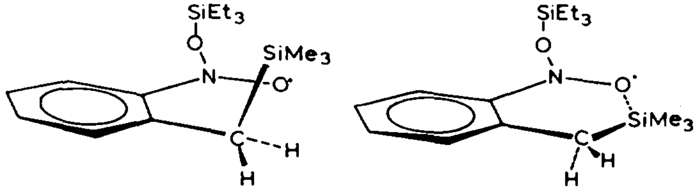
than the less electropositive X through this interaction, making the eclipsed conformation A less favoured.

(b) Since *N*-oxyls are isoelectronic with ketyls, a similar interaction to that found for ketyls may exist for *N*-oxyls. Particularly, silicon-oxygen non-bonded interaction has been proposed for the abnormal spectral properties and reactivities of β-ketosilanes [9], and it may result in the preferred conformation B. Silicon-oxygen non-bonded interaction may require the participation of vacant σ^*- or 3*d*-orbitals of silicon.

The model (a) may be unlikely. If the hyperconjugative interactions are totally repulsive in *N*-oxyls, **1d**, with a more electropositive β-substituent than a silyl group, should favour conformation B more than **1c** does. However, the observed *R* value for **1d** was even smaller than that for **1c**, i.e., 0.92. Therefore, we can regard the hyperconjugation between C–X σ-bond and N–O $p\pi$ orbitals as a totally attractive one. This strongly suggested that the staggered conformation B becomes favourable according to model (b) interactions for β-trialkylsilyl-substituted *N*-oxyls. Such an interaction may be rather weak but could well be detected by ESR spectroscopy.

In relation to this observation, we have investigated the possibility of a similar type of non-bonded interaction in (*o*-trimethylsilylmethylphenyl)triethylsiloxyamine-*N*-oxyl (**10**) involving a six-membered cyclic arrangement. The hfsc's of **10**, which was generated by the photolysis of a mixture of (*o*-trimethylsilylmethyl)nitrobenzene and triethylsilane at −50°C [10], were found to be $a_N = 15.3$, $a^H_{CH_2} = 2.04$, $a^H_{o,p\text{-H}} = 3.06$, and $a^H_{m\text{-H}} = 1.01$ G. These are compared with the values of $a^N = 15.5$, $a^H_{CH_3} = 2.91$, $a^H_{o,p\text{-H}} = 2.91$, and $a^H_{m\text{-H}} = 1.05$ G for *o*-tolyltriethylsiloxyamine-*N*-oxyl (**11**). The preferred conformation of **10** can be deduced from a comparison of benzylic proton hfsc's for **10** and **11**, and it is **10a** rather than **10b** in Scheme 4; no O–Si non-bonding interaction was detected in this case.

SCHEME 4



(10a) (10b)

Solvent effects on the preferred conformations of ***6a–6c***

It has been known that a_N values for *N*-oxyls are sensitive to the polarity of the solvent. Thus the greater the polarity of the solvent, the higher the electron density on oxygen becomes, i.e., the more spin resides on the nitrogen than on the oxygen of the N–O bond. In this context, Knauer and Napier [11] have recently proposed a_N values for di-t-butylamine-*N*-oxyl (**12**) in solvents as a useful parameter of solvent polarity. Since aniline-*N*-oxyls **6a–6c** give good ESR spectra in a wide variety of solvents, we can investigate the solvent effects on both a_N and $a^H_{\beta\text{-CH}_2}$ for these *N*-oxyls. As expected, the values of a_N for **6a–c** were found to give a linear plot, with a positive slope, against the a_N values for **12** in various solvents.

Increase in the spin density on the nitrogen (ρ_N) with increasing solvent polarity would be expected to increase also the magnitude of $a^H_{\beta\text{-CH}_2}$ on the basis of McConnell-Heller's equation (eq. 5), if the time-averaged conformation of the $X{-}CH_2$ group does not depend on the solvent. The above condition is attained with *N*-methylaniline-*N*-oxyl. Actually, $a^H_{CH_3}$ values of **6a** were found to increase roughly linearly with increasing a_N values in various solvents as shown in Fig. 6, while the $a^H_{CH_2}$ vs. a_N relationship is intricate for **6b**.

On the other hand, the situation was remarkably changed for **6c**. Thus, the $a^H_{CH_2}$ values of **6c** correlate with a_N values linearly but with opposite sign to that for **6a**. These results show that a significant dependence of the conformational preference on solvent polarity exists. The increased polarity of an N–O bond in a polar solvent may favor the eclipsed conformation A due to the enhanced hyperconjugative attraction. However, the possibility that specific solvation of the N–O bond can hinder the weak intramolecular Si ··· O non-bonded interaction and reduces the $a^H_{CH_2}$ values in polar solvents cannot be excluded at the moment.

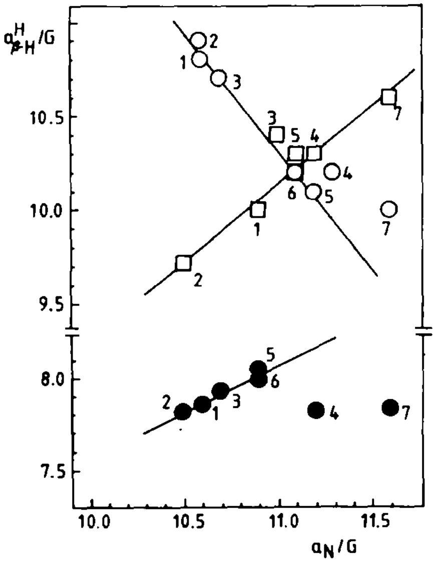


Fig. 6. Plots of $a^H_{\beta\text{-H}}$ values against a^N values for *N*-methylaniline-*N*-oxyl (□), *N*-ethylaniline-*N*-oxyl (●), and *N*-trimethylsilylmethylaniline-*N*-oxyl (○) in the solvents CCl_4 (1), diethyl ether (2), benzene (3), chloroform (4), dichloromethane (5), acetonitrile (6), and methanol (7).

Unrestricted CNDO/2 calculations of silylmethylamine-N-oxyl

As described above, it is attractive to attribute the observed anomalous preference of the conformation in trialkylsilylmethylamine-*N*-oxyls to the contribution of the Si–O non-bonded interaction. Unrestricted CNDO/2 molecular orbital calculations [12] may be a useful tool to provide further information about the conformational implication of this. The calculations for the parent silylmethylamine-*N*-oxyl (**13**) were carried out as a function of the parameters; l_{NC}, the length of the N–C bond, and α, the angle of rotation around the N–C bond (cf. Fig. 7). The following assumptions were made concerning the structure of this radical: it has a tetrahedral arrangement of the silyl protons about the axis of the Si–C bond, and a planar and trigonal radical site. Other parameters are given in Fig. 7.

The calculated total energy of **13**, relative to that when the value for $\alpha = 0°$, are plotted in Fig. 7 as a function of α (for $l(NC) = 1.55$ and 1.47 Å, respectively). A number of features emerge. When *d*-functions were not included in the basis set for

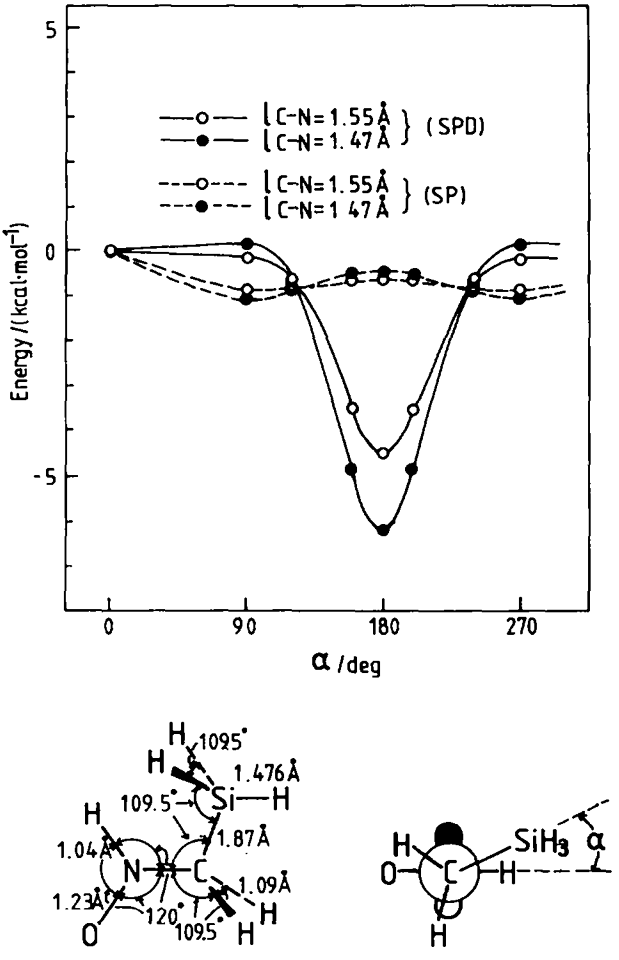


Fig. 7. Plots of total energies of silylmethylamine-*N*-oxyl as a function of α calculated by CNDO/2; bond lengths and bond angles used for the calculation are shown under the graph.

silicon [13], the conformation A (R = H, X = SiH_3), in Scheme 2, $\alpha = 90°$, was the most stable (as expected from the theory of hyperconjugation), while the rotational barrier was rather small ($\Delta E = 0.85$ kcal/mol for l(NC) = 1.55 Å and $\Delta E = 1.05$ kcal/mol for l(NC) = 1.47 Å). On the other hand, the conformation B, $\alpha = 180°$, was considerably stabilized ($\Delta E = 4.5$ kcal/mol for l(NC) = 1.55 Å and $\Delta E = 6.2$ kcal/mol for l(NC) = 1.47 Å) when *d*-functions were included in the basis set for silicon. Since no attempt was made to optimize the geometries and the CNDO/2 method is known to overestimate the role of *d*-orbitals, these calculations should be regarded only as suggestive. Nevertheless, it is important to note that the calculations qualitatively explain the conformational anomaly shown by silylmethylamine-*N*-oxyls only in case of the calculations with an *spd* basis set. These results suggest strongly the presence of significant non-bonding attraction between the N–O bond and the silyl group, due to Si *d*- (and/or σ^*) orbital participation, although the specific role of the orbital is still unclear.

Experimental

Materials

N-Methylaniline, *N*-ethylaniline, diethylamine, dimethylamine, and *m*-chloroperoxybenzoic acid were commercially available. *N*-(Trimethylsilylmethyl)aniline [14], *N*-(dimethylphenylsilylmethyl)aniline [15], bis(trimethylsilylmethyl)amine [14], bis(dimethylphenylsilylmethyl)amine [14], methyl(trimethylsilylmethyl)amine [14], t-butylmethylamine [16], t-butylethylamine [17], and methylethylamine [18] were prepared by the reported procedures. All the samples were purified by fractional distillation. All the solvents for ESR measurements were purified by the usual procedures.

t-Butyl(trimethylsilylmethyl)amine

The mixture of t-butylamine (5.49 g, 0.075 mol) and iodomethyltrimethylsilane (5.35 g, 0.025 mol) was heated at about 137°C in an autoclave (50 ml) for 8 h. After washing the reaction mixture with 15% aq. NaOH (50 ml), usual work-up gave 2.58 g (65%) of t-butyl(trimethylsilylmethyl)amine: b.p. 65–77°C (90 mm Hg); ^{1}H NMR (CCl_4) δ: -0.10 (s, 9H), 0.92 (s, 9H), 1.85 (s, 2H). Anal.: Found: C, 60.16; H, 13.26; N, 8.51. $C_8H_{21}NSi$ calcd.: C, 60.30; H, 13.28; N, 8.79%.

Methyl(trimethylgermylmethyl)amine

The mixture of chloromethyltrimethylgermane (2.52 g, 0.015 mol) and anhydrous methylamine (7.0 ml, 0.15 mol) was heated at 125°C for 4 h in an autoclave (50 ml). After work-up, 1.25 g (51%) of methyl(trimethylgermylmethyl)amine was obtained: b.p. 52–68°C. An analytical sample, was obtained by preparative GLC (column, SE-30, 30%, 2 m); ^{1}H NMR ($CDCl_3$) δ: 0.26 (s, 9H), 1.26 (br-s, 1H), 2.22 (s, 2H), 2.41 (s, 3H); MS m/e 162 (M^+). Anal: Found: C, 37.22; H, 9.43; N, 8.68. $C_5H_{15}NGe$ calcd.: C, 37.12; H, 9.35; N, 8.68%.

ESR measurements

A Varian E-12 spectrometer (X band) with 100 kHz modulation frequency was used for the ESR measurements. Photolysis was carried out in the cavity of the ESR spectrometer by an Ushio super-high pressure 500 W mercury lamp.

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