JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 197–207 (1988)

ELECTRON SPIN RESONANCE STUDY ON RADICALS STABILIZED BY THE σ–π CAPTODATIVE EFFECT[1]

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ABSTRACT

ESR spectra of 1-cyano-2-(trimethylsilyl)ethyl and related radicals were recorded. Temperature dependent ESR spectra of these radicals revealed that electron-releasing trimethylsilylmethyl and electron-withdrawing cyano groups synergetically functioned to stabilize the radical centers due to σ–π captodative effects.

INTRODUCTION

It has been demonstrated that radicals having an Si atom at the β-position are stabilized by σ–π conjugation, although the magnitude of this interaction is estimated to be relatively small.

In a previous paper, we have reported that a combination of trimethylsilylmethyl and cyano groups exerts an enhanced radical stabilizing influence due to the σ–π captodative effect.[2] In the 1-cyano-2-(trimethylsilyl)ethyl radical (1), the interaction between the σ(Si—C) and the SOMO 2*p* orbitals is considered to be larger than that oberved in the 2-(trimethylsilyl)ethyl radical (2), since the energy level of the 2*p* orbital in **1** is lowered in some extent due to the interaction with the π* orbital of the cyano group as shown in Figure 1.

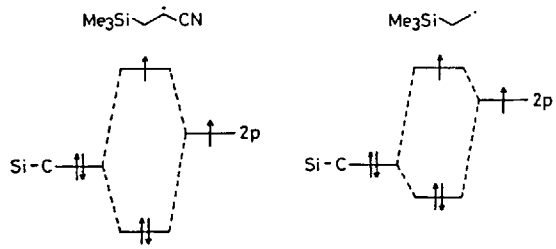

Figure 1. Interaction of σ(Si—C) and 2*p* orbitals in 1-cyano-2-(trimethylsilyl)ethyl (**1**) and 2-(trimethylsilyl)ethyl (**2**) radicals

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0894–3230/88/040197–11$05.50

Received 10 November 1987
Revised 10 February 1988

One possible way of estimating the magnitude of such an effect may be provided by ESR measurements. For example, l-(trimethylsilylmethyl)allyl[3] and 1,3-bis(trimethylsilyl)-2-propyl radicals[4] were studied by ESR and the magnitude of σ–π conjugation was analyzed in terms of their conformation and rotation barriers. In this paper, we present some ESR experimental evidence for such an effect on σ–π stabilized radicals.

RESULTS AND DISCUSSION

Generation and ESR Spectra of Radicals

l-Cyano-2-(trimethylsilyl)ethyl and related radicals (**1**, **3**, **4**) were generated by addition of the trimethylsilyl radical to substituted acrylonitriles. Thus photolysis of solutions of di-*t*-butyl peroxide (DTBP), trimethylsilane, and an acrylonitrile derivative in cyclopropane gave well defined ESR spectra. The temperature-dependent ESR spectra of **1** and **4** are shown in Figures 2 and 3, respectively, together with simulated spectra.

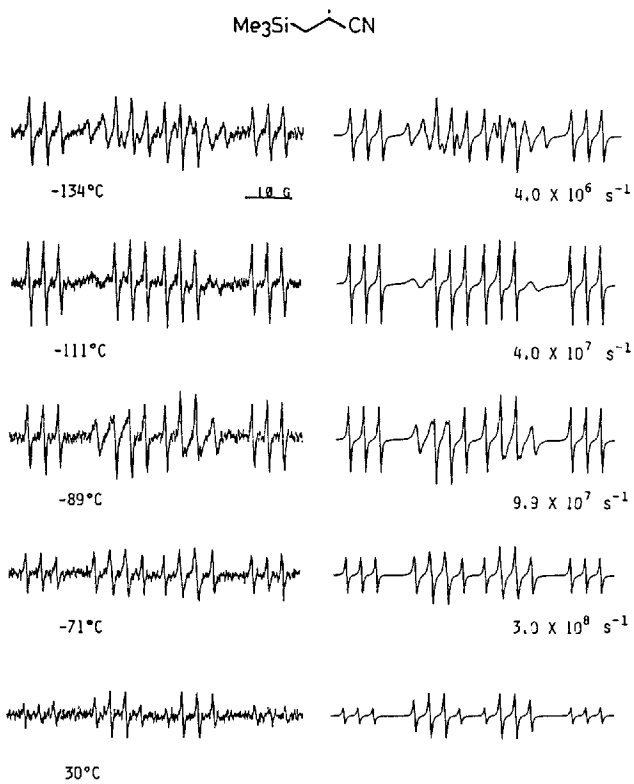


Figure 2. The temperature-dependent ESR spectra of **1** (left) and computer-simulated spectra obtained with the designated rate constants (right)

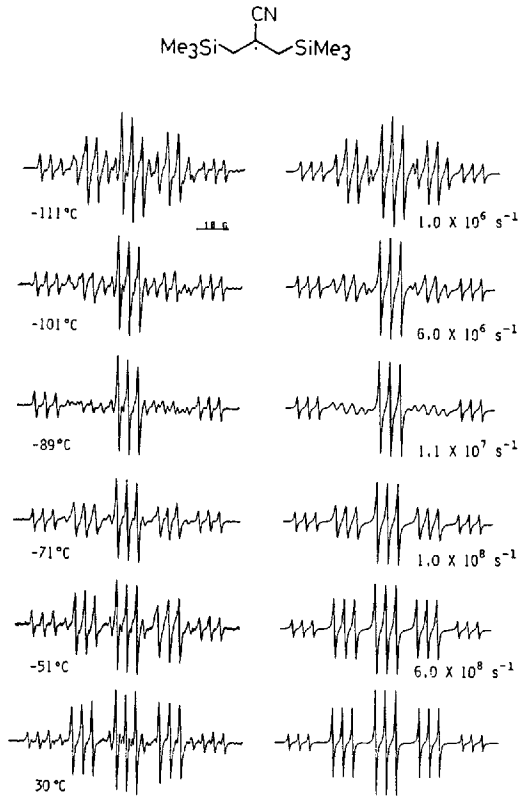
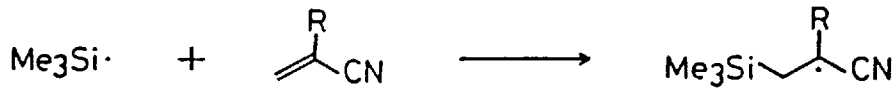


Figure 3. The temperature-dependent ESR spectra of **4** (left) and computer-simulated spectra obtained with the designated rate constants (right)



1: R = H **3**: R = Me **4**: R = CH_2SiMe_3

At −134 °C two methylene protons of **1** have different coupling constants, and its ESR spectrum consists of a doublet of doublets of doublets which further splits into triplets by nitrogen. As the temperature rises, selective line-broadening occurs, and at −71 °C the spectrum shows a pattern of a doublet of triplets of triplets. This change can be attributed to freezing the free rotation of the Si—C(β) bond. Similarly ESR spectra of **4** show a triplet of triplets of triplets at low temperatures, and a quintet of triplets at high temperatures. These radicals are relatively stable and can be observed even at room temperature.

The ESR spectrum of **3** at −91 °C is shown in Figure 4. At this temperature, two methylene protons become nearly equivalent and the spectrum consists of a quartet of triplets of triplets. The values of hyperfine splitting constants (hfsc) of these radicals together with literature values are listed in Table 1.

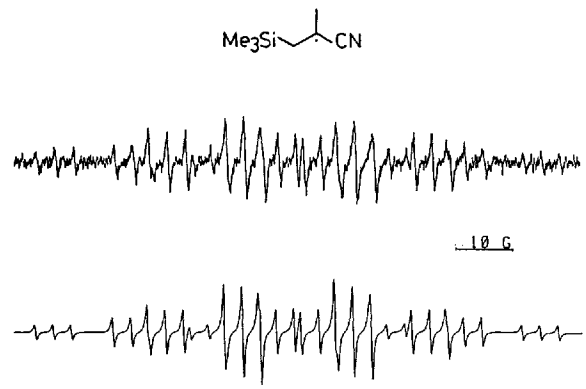


Figure 4. The ESR spectrum of **3** at −91 °C (above) and the simulated spectrum (below)

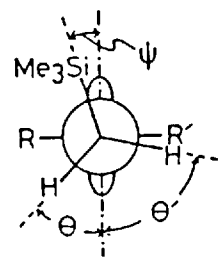
Table 1. Proton hfsc's of 1-substituted 1-cyano-2-(trimethylsilyl)ethyl and related radicals, $MCH_2\dot{C}RCN$

Radical	M	R	T/°C	$a(\alpha)/G$	$a(\beta)/G$	$a(N)/G$	Reference
5	H	H	25	19.65	23·05	3·48	5
1	$SiMe_3$	H	−134	19·0	12·7,16·8	3·3	this work
			30	19·0	15·6	3·3	"
3	$SiMe_3$	Me	−91	19·6[a]	13·6	3·2	"
4	$SiMe_3$	CH_2SiMe_3	−111		11·0,14·3	3·2	"
			30		13·6	3·2	"

[a]Methyl proton hfsc.

Preferred Conformation of the Radicals at Low Temperatures

The degree of σ–π conjugation of 2-silylethyl radicals is considered to be most effective in the bisected conformation. Indeed, preferred conformations of several 2-silylethyl radicals have been determined by ESR and reported to be nearly bisected ones.[3,4] As the dihedral angle ψ becomes smaller, overlap between the Si—C bond and the p orbital becomes more efficient. Therefore, the dihedral angle can be regarded as a measure of the degree of σ–π conjugation.



Conformational analysis of the radicals is carried out using the simple $\cos^2\theta$ rule for the β-proton coupling[6] (equation 1) and the McConnell relation for the α-proton coupling[7] (equation 2), where ρ is the π spin density on the radical center and B and Q are constants. Equation 3 is derived from equations 1 and 2.

$$a(\beta) = B\rho\cos^2\theta \quad (1)$$

$$a(\alpha) = Q\rho \quad (2)$$

$$\theta \text{ or } \theta' = \cos^{-1}\left(\frac{Qa(\beta)}{Ba(\alpha)}\right)^{\frac{1}{2}} \quad (3)$$

The value of B/Q is estimated to be 2·346 from the value of hfsc's of the 2-propionitrile radical (**5**),[5] where $\cos^2\theta$ for a freely rotating methyl group is 0·5. For the radical **4**, θ is calculated using equation 4, where the value of $B\rho$ is estimated to be 39·2 from $a(CH_3)$ of the 2-cyano-l-trimethylsilyl-2-propyl radical **3**. The dihedral angle ψ is calculated from equation 5 by assuming that C(α)—C(β)−M planes bisect the H(β)—C(β)—H′(β) angles. The calculated values of θ, θ', and ψ are listed in Table 2.

$$\theta \text{ or } \theta' = \cos^{-1}\left(\frac{a(\beta)}{B\rho}\right)^{\frac{1}{2}} \quad (4)$$

$$\psi = \frac{\theta' - \theta}{2} \quad (5)$$

These values together with consideration of the steric repulsion between the $SiMe_3$ group and substituent(s) on C(α), suggest the orientation of the $SiMe_3$ group in the preferred conformation to be shown in Figure 5.

The most stable conformations of other 2-silylethyl radicals (**6** and **7**) reported earlier[3,4] are also listed in Table 2, and are illustrated in Figure 6. The substituents on C(α) in **7**, **6**, and **1** refer to the C (conjugated), X (electron-releasing), and Z (electron-withdrawing) substituents according to Houk's classification.[8,9] Among these, **1** has the most effective overlap between σ(Si—C(β)) and 2*p* orbitals. Since the relative energy levels of σ(Si—C(β)) and 2*p* orbitals are considered as shown in Figure 7,[9] interaction betwen σ(Si—C(β)) and 2*p* orbitals with the CN substituent is the strongest even if ψ's were the same among **1**, **6**, and **7**. Therefore, σ–π conjugation of **1** is considered to be stronger than that of systems with C or X substituents.

Spin Density at Radical Centers

Relative stability of radicals having a similar structure can be evaluated by the degree of delocalization of the odd electron, that is, spin density at radical centers. A recent study on the captodative radicals has revealed that the combined action of electron-withdrawing and electron-releasing groups shows enhanced decrease on spin density.[10a,11,12] Therefore, one of

Table 2. Dihedral angles in the preferred conformations of substituted 2-(trimethylsilyl)ethyl radicals, $Me_3SiCH_2\dot{C}RR'$

Radical	R	R′	T/°C	θ	θ'	ψ	Reference
1	H	CN	−134	52·1	57·7	2·8	this work
4	CN	CH_2SiMe_3	−111	52·8	58·0	2·6	"
6	H	CH_2SiMe_3	−158	48·6	58·8	5·1	4
7	H	$CH{=}CH_2$	−173	45	65	10	3

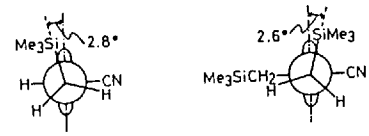


Figure 5. The preferred orientation of the trimethylsilyl group against the substituent(s) on the radical center

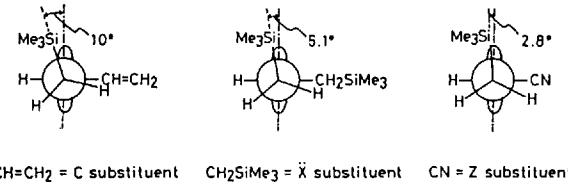


Figure 6. Comparison of ψ's of 2-silylethyl radicals having different kinds of substituents

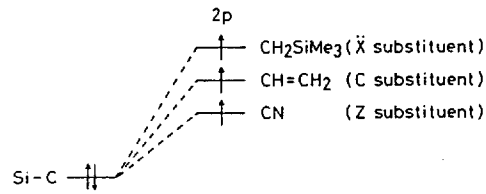


Figure 7. Interaction of σ(Si—C) and $2p$ orbitals in l-substituted 2-(trimethylsilyl)ethyl radicals

the best ways to examine whether the captodative effect is operative for a radical may be provided by measuring the spin density of the radical in question.

The spin density is related to the hfsc of α-protons and can be calculated by equation 2, where Q is 23·0 (G) in the case of planar radicals. Since the cyano group has been reported to induce a planar configuration at radical centers,[13] and σ–π conjugation in the 2-silylethyl radical is considered to be most efficient when the radical center is planar, it is assumed that all the radicals in Table 3 have planar configuration. Therefore, the spin densities in a series of radicals in Table 3 can be compared each other by using values of $a(\alpha)$. Substitution of both

Table 3. α-Proton hfsc's of substituted methyl radicals, HĊRR′

Radical	R	R′	T/°C	$a(\alpha)/G$	Reference
8	H	H	−177	23·04	14
2	CH_2SiMe_3	H	−112	21·05	15
9	CN	H	25	20·88	5
6	CH_2SiMe_3	CH_2SiMe_3	− 78	20·20	4
10	CN	CN		19·6	5
1	CH_2SiMe_3	CN	−134	19·0	this work

trimethylsilylmethyl and cyano groups decreases the spin density and the effect is larger for the cyano group (**2**, **9**). Introduction of a second group with a similar donor–acceptor character further decreases the spin density (**6**, **10**), but in a diminished degree compared with the first introduction (**2**, **9**). When trimethylsilylmethyl and cyano groups are introduced simultaneously at the radical center like in **1**, the spin density becomes smaller than that of **6** and **10**. These results are compatible with the concept of the captodative effect.

Next, we will discuss the extent of spin delocalization in 1-substituted ethyl radicals, $CH_3\dot{C}RR'$ by using ESR parameters in order to obtain further information on spin coupling constants due to the methyl group. When α-proton of the ·CHRR′ radicals is replaced by a methyl group, the spin density can be calculated by the relation of the coupling constant for the methyl group and the spin density on the radical center (equation 6).[16] On the other hand, the spin density (ρ_{calc}) may be estimated by equation 7 as suggested by Fessenden and Schuler, since a substituent R_i attached to the radical center reduces the spin density on that center by a constant fraction $\Delta(R_i)$.[16]

$$a(CH_3) = 29{\cdot}30\rho_{obs} \tag{6}$$

$$\rho = \sum_{i=1}^{3} \{1 - \Delta(R_i)\} \tag{7}$$

Values of ρ_{obs} are listed in Table 4 and values of $\Delta(R)$[17] of trimethylsilylmethyl and cyano groups are calculated by using ρ_{obs} of **11** and **5**. The value of $\Delta(CH_3) = 0{\cdot}081$, are also listed. The values of ρ_{calc} of **12** and **3** are calculated with these $\Delta(R)$'s, and listed in Table 4. Good agreement between calculated and observed values of spin densities is noted. However, ρ_{obs} of **3** is smaller by 0·041 than ρ_{calc}. This means that the degree of spin delocalization in **3** is more extensive than the expected effects by a simple combination of trimethylsilylmethyl and cyano groups. In other words, both substituents function clearly cooperatively for the captodative effect.

Barriers to Rotation

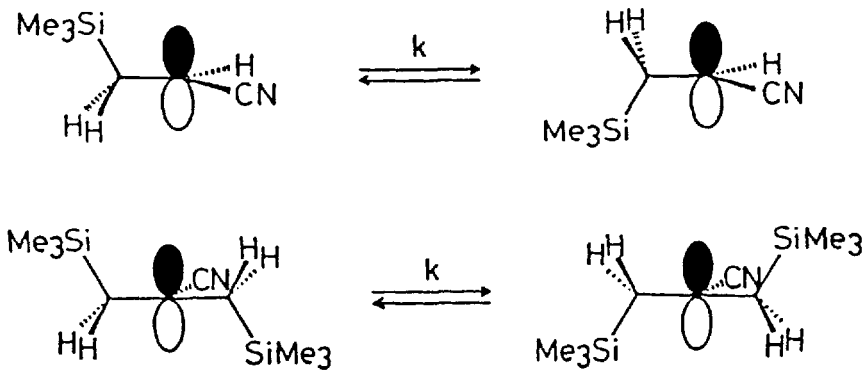
In 2-silylethyl radicals, stabilization energy by σ–π conjugation is maximum in the eclipsed conformation and is minimum in perpendicular conformation between the silyl group and the π SOMO. Rotational barriers of the Si—C(β) bond around the C(α)—C(β) bond can therefore be regarded roughly as the stabilization energy by σ–π conjugation.

As shown in Figures 2 and 3, freezing of rotation of the trimethylsilyl groups in **1** and **4** is observed in the temperature dependent ESR spectra simulated by assuming the two-jump

Table 4. Spin density of the radical center in 1-substituted ethyl radicals, $CH_3\dot{C}RR'$

Radical	R	R′	T/°C	$a(CH_3)/G$	ρ_{obs}	$\Delta(R)$	ρ_{calc}	Reference
11	CH_2SiMe_3	H	−60	24·3	0·829	0·098	–	18
5	CN	H	25	23·05	0·787	0·144	–	5
12	CH_2SiMe_3	CH_2SiMe_3	−81	21·85	0·746	–	0·748	4
3	CH_2SiMe_3	CN	−91	19·6	0·669	–	0·710	this work

model. The rate constants of exchange (k) are determined by comparison of the experimental spectra with the simulated ones.



The plots of ln k vs. T^{-1} and ln k/T vs. T^{-1} are shown in Figure 8. Activation parameters were determined using the following equations and listed in Table 5.

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{8}$$

$$\ln \frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln \frac{k}{h} \tag{9}$$

$$\Delta G^{\ddagger} = RT\left(\ln \frac{k}{h} T - \ln k\right) \tag{10}$$

Unfortunately, the activation parameters of the unsubstituted 2-(trimethylsilyl)ethyl radical have not been reported, and therefore, it is impossible to estimate the increment of E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ of **1** due to the introduction of a cyano group. However, the comparison of the parameters of **1** with **6** and **7** reveals that E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ of **1** is significantly larger than those of C- and X-substituted radicals. Therefore, σ–π conjugation in the presence of a cyano group is found to be stronger than those of unsubstituted 2-silylethylradicals.

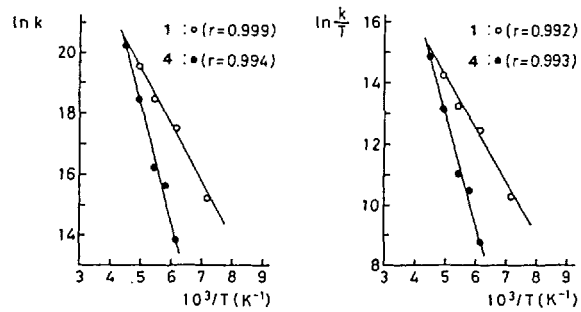


Figure 8. Plots of ln k vs. T^{-1} and ln k/T vs. T^{-1} for the hindered rotation about the C(α)—C(β) bond of radicals **1** and **4**

Table 5. Comparison of the activation parameters for the hindered rotation about the C(α)—C(β) bond of radicals

Radical		E_a[a]	log$A$	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	$\Delta G^{\ddagger}_{173K}$[a]	Reference
Me_3Si(CN)	(1)	3·7	12·5	3·4	−2·3	3·8	this work
Me_3Si($SiMe_3$)	(6)	3·0	12·3	2·7	−2·7	3·2	4
Me_3Si(=)	(7)	3·1	12·6				3
Me_3Si(CN)($SiMe_3$)	(4)	7.4	16·0	7·0	13·6	4·7	this work
Me_3Si($SiMe_3$)($SiMe_3$)	(12)	8·8	18·1	8·5	23·2	4·5	4

[a]kcal mol^{-1}
[b]cal mol^{-1} K^{-1}

In the case of **4**, E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}_{173K}$ are far larger than those of **1**. This may partly be explained by the steric effect of the cyano group because of the flip–flop motion of the radical should be considered to proceed with a non-concerted correlated mode (Figure 9) and one trimethylsilyl group must interact with the cyano group in this process. Equation 11 is used to evaluate the increment of $\Delta G^{\ddagger}$ by the steric effect, as it has been successfully applied to 2,2′-disubstituted biphenyl and other systems.[19]

$$\Delta G^{\ddagger}_{340K}(\text{kJ mol}^{-1}) = 26\Sigma r^{*} + 4{\cdot}7 \tag{11}$$

Apparent overlap of the van der Waals radius r^{*} was calculated using appropriate bond lengths, angles and van der Waals radii shown in Figure 10. With these values, the increment of $\Delta G^{\ddagger}_{340K}$ for the steric effect was calculated from equation 11 and found to be $\Delta\Delta G^{\ddagger}_{340K}$(Me—H) = 2·0 (kcal/mol) and $\Delta\Delta G^{\ddagger}_{340K}$ (CN—H) = 1·3 (kcal/mol). Although these

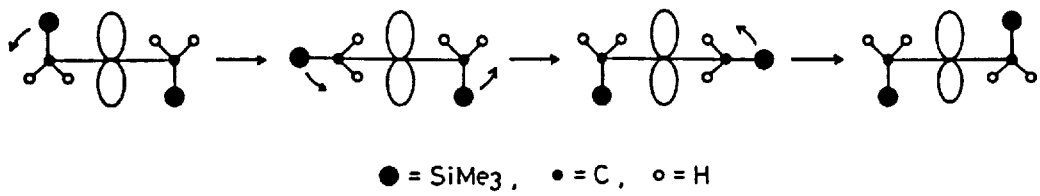


Figure 9. Mechanism for the flip–flop motion of 1,3-disubstituted 2-propyl radicals

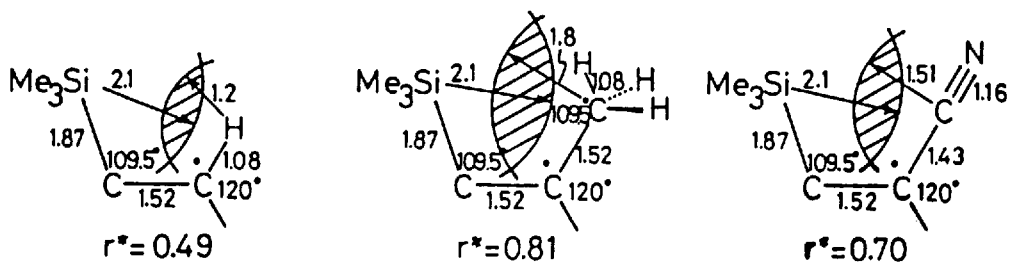


Figure 10. Overlap of the van der Waals radii of the trimethylsilyl group and a substituent on C(α) in the process of the flip–flop motion of 1,3-disubstituted 2-propyl radicals

values are calculated at different temperatures, it is reasonable to assume that the increment of $\Delta G^{\ddagger}_{173K}$ for the steric effect is largest in the case of the methyl group among others.

The unusual increment of $\Delta G^{\ddagger}_{173K}$ of **4** may also indicate the existence of σ–π conjugation enhanced by the captodative effect in addition to the steric repulsion. However, further discussion of the activation parameters may not be relevant because of the uncertainty of the figures.

In conclusion, temperature dependent ESR spectra of a series of radicals provided a strong support for the σ–π captodative effect.

EXPERIMENTAL

Materials

Trimethylsilane (Petrarch Systems Inc.) and cyclopropane (Takachiho Chemical Inc.) were obtained commercially and used without further purification. Acrylonitrile and methacrylonitrile were obtained commercially and distilled before use. Di-*t*-butyl peroxide (DTBP) was purified according to literature.[3]

ESR Measurement

A mixture of a nitrile, trimethylsilane, DTBP, and cyclopropane (v/v 1:4:2:4) was degassed and irradiated by a 500 W super-high pressure mercury lamp (Ushio) in a cavity of a Varian E-12 ESR spectrometer. Temperatures were controlled by a Varian variable temperature apparatus and calibrated by a Cu-constantane thermocouple to within ± 2 °C.

Simulation

Computer simulation was carried out with the program of ESREXN (QCPE No. 209) at the Calculation Center of Tohoku University.

REFERENCES

1. *Chemistry of Organosilicon Compounds, No. 244.*
2. H. Sakurai, S. Kyushin, and Y. Nakadaira, *Chem. Lett.*, 297 (1987).
3. T. Kawamura, P. Meakin, and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 8065 (1972).
4. M. Kira, M. Akiyama, and H. Sakurai, *J. Organomet. Chem.*, **271**, 23 (1984).
5. P. Smith *et al.*, *J. Magn. Res.*, **18**, 254 (1975).
6. H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).
7. C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).
8. K. N. Houk, *J. Am. Chem. Soc.*, **95**, 4092 (1973).
9. I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley-Interscience, Chichester (1976).
10. (a) H. G. Viehe, Z. Janousek, and R. Merenyi, *Acc. Chem. Res.*, **18**, 148 (1985). (b) H. G. Viehe, R. Merenyi, L. Stella, and Z. Janousek, *Angew. Chem., Int. Ed. Engl.*, *18*, 917 (1979).
11. L. Sylvander, L. Stella, H. -G. Korth, and R. Sustmann, *Tetrahedron Lett.*, 749 (1985).
12. H.-G. Korth, P. Lommes, and R. Sustmann, *J. Am. Chem. Soc.*, **106**, 663 (1984).
13. R. A. Kaba and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 523 (1976).
14. R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

15. T. Kawamura and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 648 (1972).
16. R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
17. H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964); **20a**, 428 (1965).
18. M. Kira, H. Osawa, and H. Sakurai, *J. Organomet. Chem.*, **259**, 51 (1983)
19. G. Bott, L. D. Field, and S. Sternhell, *J. Am. Chem. Soc.*, **102**, 5618 (1980).