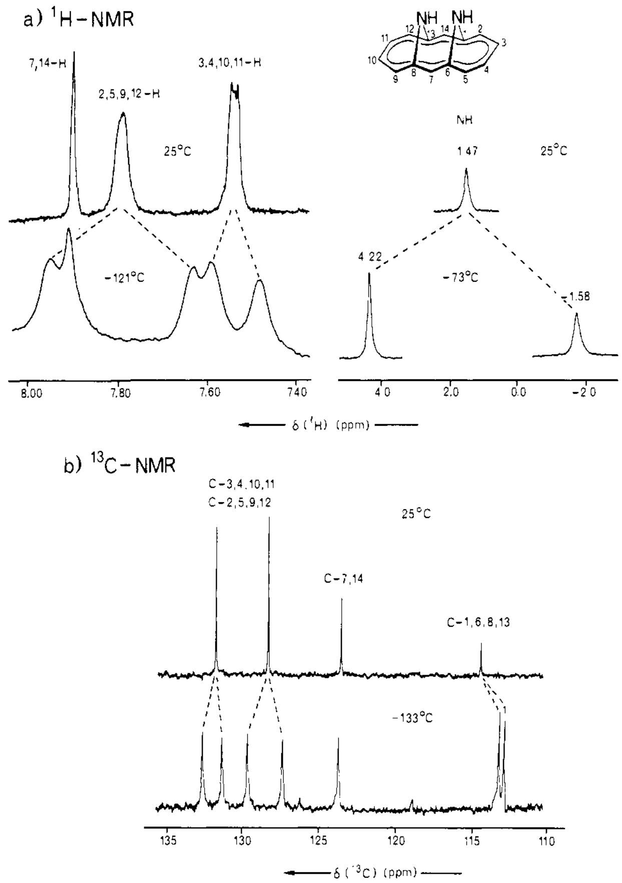

Figure 1. (a) 400-MHz ^{1}H NMR (25 °C, 0.2 M in $CDCl_3/CCl_4$ 10:1; low temperature, 0.1 M in CD_2Cl_2/C_2H_5Cl 2:1); (b) 100-MHz ^{1}H-decoupled ^{13}C NMR (25 °C, 0.07 M in CD_2Cl_2; −133 °C, 0.1 M in CD_2Cl_2/C_2H_5Cl 2:1).

sole isolable product (mp 170 °C, dec; 56%). As anticipated, reduction of **4** with lithium aluminum hydride furnished **5** (mp 83 °C; 75%). When **5** was treated sequentially with bromine in dichloromethane and sodium methoxide in THF, 7,14-dihydro-*syn*-1, 6:8,13-diimino[14]annulene (mp 145 °C), a bis(1*H*-azepine), was obtained[8] but the dehydrogenation of this chemically capricious molecule led to complex mixtures of products. In order to avoid the intermediacy of the 7,14-dihydro derivative of **1**, the bis(aziridine) **5** was protected as its sulfinamide **6** (mp 204–205 °C; 65%). Application of the bromination–dehydrobromination reaction sequence to **6** provided **7**, which after isolation by chromatography was treated with 2,3-dichloro-5,6-dicyanobenzoquinone to give **8** [26%, based on **6**]. The protection method employed with **5** served admirably, since **1** was smoothly liberated from **8** by acid hydrolysis. After crystallization from benzene, **1** was obtained as air-stable scarlet red prismatic crystals [mp 158 °C; 65%; UV (methanol) 305 (ϵ 105 700), 340 sh (12 400), 376 (8400), 532 nm (700); IR (CsI) 3170, 3038, 1531 cm^{-1}; as determined spectrophotometrically, **1** behaves as a monoamine toward perchloric acid exhibiting a pK_a of 5.74].[9]

The structure and dynamic behavior of **1** follow from NMR spectroscopic studies. In the ^{1}H NMR spectrum at room temperature, the annulene protons give rise to a singlet at δ 7.89 (H-7,14) and an AA′BB′ system at δ 7.80 (H-2,5,9,12) and 7.53 (H-3,4,10,11) (J_{23} = 8.86, J_{34} = 9.62 Hz), whereas the NH protons appear as a broadened singlet at δ 1.47 (Figure 1a). As indicated by both the chemical shifts and the coupling constants, **1** must possess a delocalized π-electron system.[10] Dynamic behavior of **1** is revealed by the reduced spectral symmetry on lowering the temperature: at −100 °C two AA′BB′ systems and two NH signals [δ 4.22 (H_{endo}) and −1.58 (H_{exo})] occur. Correspondingly, the four signals observed in the ^{13}C NMR spectrum at room temperature [δ 114.21 (C-1,6,8,13), 128.42 (C-2,5,9,12), 131.90 (C-3,4,10,11), 123.55 (C-7,14)] increase to seven in the slow exchange limit at −133 °C (Figure 1b). Evidence that the dynamic process in question is the configurational inversion of the nitrogen atoms (**1a** $\rightleftarrows$ **1b**) is provided by the following findings: (1) the ^{1}H and ^{13}C NMR signals of H-7,14 and C-7,14, respectively, remain unaffected as the temperature is decreased; (2) in hydrogen-bonding solvents such as CH_3OD the coalescence temperature, and hence the barrier of the process, is raised; (3) the occurrence of a π-bond shift, while being compatible with the changes in the ^{13}C NMR spectrum, is ruled out by the characteristic features in the ^{1}H NMR spectrum.[11] A line shape analysis of the three two-site exchange systems encountered in the ^{13}C NMR spectrum afforded $\Delta H^{\ddagger}$ = 26.1 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −76.5 J mol^{-1} K^{-1} for the inversion of the nitrogen atoms (**1a**) $\rightleftarrows$ (**1b**), which is assumed to be synchronous.[12] The intramolecular nature of this inversion derives from the observation that the rate constants are not dependent on concentration within experimental error.[13]

Acknowledgment. J. A. Marco thanks the Alexander von Humboldt-Foundation for a fellowship.

Registry No. 1, 75863-17-1; *syn*-**2**, 10133-47-8; *anti*-**2**, 5910-29-2; **3**, 87533-11-7; **4**, 87533-12-8; **5**, 87533-13-9; **6**, 87533-14-0; **7**, 87533-15-1; **8**, 87533-16-2; 1,4,5,8,9,10-hexahydroanthracene, 5910-28-1; 7,14-dihydro-*syn*-1,6:8,13-diimino[14]annulene, 87533-17-3.

Supplementary Material Available: NMR, IR, and UV spectral data of intermediates **2–8** (1 page). Ordering information is given on any current masthead page.

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(8) Unpublished results with Kuebart, F.

(9) The pK_a of 1,6-imino[10]annulene is found to be 3.78: Bremser, W. Diplomarbeit, Cologne University, D-5000 Köln 41, West Germany, 1966.

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(11) The ^{1}H NMR chemical shifts and coupling constants of **1** match those of the nondynamic *syn*-1,6:8,13-diepoxy[14]annulene, which has been shown by X-ray analysis to possess a delocalized 14π-electron system.

(12) The existence of high-energy exo,exo (lone-pair repulsion) and/or endo,endo isomers (H,H repulsion) as intermediates cannot be excluded.

(13) At 200, 210, 215, 217, and 221 K the following rate constants were obtained for a 0.1 and 0.05 M solution of **1** in CD_2Cl_2/C_2H_5Cl (7:3), respectively: k (s^{-1}) 53/38, 124/105, 182/199, 228/227, 308/295.

ESR Study of Twisting in Trimethylsilyl-Substituted Alkene Cation Radicals[1]

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A number of theoretical studies predicted substantial twisting from planarity in alkene cation radicals.[2] For instance, recent MNDO-UHF calculations[2f] have shown 25° twist in the ethene cation radical and a much larger twist angle in the tetramethyl derivative. Several spectral analyses confirmed such a twisting in the ethene cation radical.[3] Although ESR is a powerful tool for investigating the electronic structure and geometry of radical

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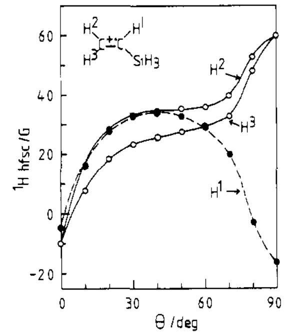
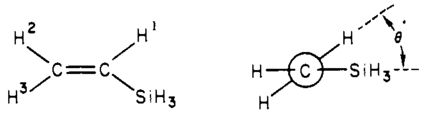


Figure 1. Dependence of olefinic proton hfsc's in vinylsilane cation radical on a twist angle around a carbon–carbon bond calculated by INDO-UHF. See in text for the calculation details.

species, so far as we know, the technique has never been applied to the problem of twisting in alkene cation radicals.

Figure 1 shows dependence of olefinic proton hyperfine splitting constants (hfsc's) on the twist angle in vinylsilane cation radical ($1^{+\cdot}$) calculated by INDO-UHF.[4] As expected, the ^{1}H hfsc's



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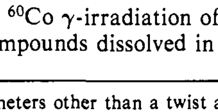
are very sensitive to the twist angle around a carbon–carbon bond (θ); hfsc's of H^2 and H^3 increase monotonously with increasing θ to reach to 60 G[5] at the perpendicular geometry, while hfsc of H^1 shows the maximum at around $\theta = 45°$.[6] The calculation suggests that the olefinic ^{1}H hfsc's should be a reliable measure of twisting in alkene cation radicals. We now report the first decisive evidence for remarkable twisting in trimethylsilyl-substituted ethene cation radicals on the basis of the unusually large hfsc's of olefinic protons.

Various trimethylsilylalkene cation radicals ($2^{+\cdot}$–$8^{+\cdot}$) were



2, $R^1 = SiMe_3$; $R^2 = R^3 = H$
3, $R^1 = SiMe_3$; $R^2 = CH_3$; $R^3 = H$
4, $R^1 = SiMe_3$; $R^2 = t\text{-Bu}$; $R^3 = H$
5, $R^1 = R^2 = SiMe_3$; $R^3 = H$
6, $R^1 = R^2 = H$; $R^3 = SiMe_3$
7, $R^1 = R^3 = H$; $R^2 = SiMe_3$
8, $R^1 = H$; $R^2 = D$; $R^3 = SiMe_3$

generated at 77 K by ^{60}Co γ-irradiation of solid solutions containing the parent compounds dissolved in $CFCl_3$.[7,8]

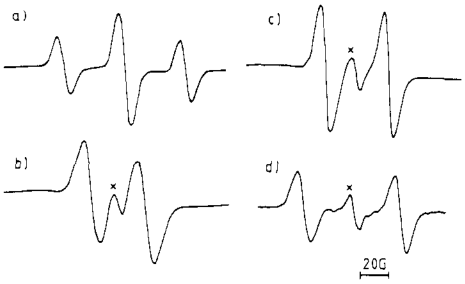


Figure 2. ESR spectra of 1,1-bis(trimethylsilyl)ethene and the 2-substituted cation radicals in $CFCl_3$: (a) $2^{+\cdot}$ at 133 K, (b) $3^{+\cdot}$ at 133 K, (c) $4^{+\cdot}$ at 133 K, (d) $5^{+\cdot}$ at 133 K. Signals due to unidentified species are denoted by x.

1,1-Bis(trimethylsilyl)ethene and its 2-substituted derivatives (**2–5**) afforded ESR spectra shown in Figure 2. The spectra did not depend essentially on temperatures in a range of 77–143 K. The ESR spectrum of $2^{+\cdot}$ consists of a triplet with the hfsc of 44.2 G ($g = 2.0038$).[9] This large ^{1}H hfsc can be unequivocally assigned to the two equivalent olefinic protons since the trisubstituted ethene cation radicals ($3^{+\cdot}$, $4^{+\cdot}$, and $5^{+\cdot}$) gave ESR of doublet patterns with comparably large hfsc's (g values in parentheses) of 39.0 (2.0033), 45.3 (2.0031), and 64.5 G (2.0033), respectively. According to the dependence of olefinic proton hfsc's on twist angles calculated by INDO, such unusually large ^{1}H hfsc's should indicate significant twisting in trimethylsilyl-substituted ethene cation radicals compared with common alkene cation radicals where the olefinic proton hfsc's are recorded in the magnitude of around 10 G.[7]

Since the hfsc's appear to increase with increasing size of substituents at the 2-position in the 2-substituted-1,1-bis(trimethylsilyl)ethene cation radicals, a simple steric effect to increase twisting could be responsible for large hfsc values. However, such a very large hfsc was observed even in $2^{+\cdot}$, where no significant vicinal steric strain is expected in the planar structure. Therefore, enhanced σ–π conjugation by trimethylsilyl substituents[10] can be a major factor to increase and stabilize twisted structures in silyl-substituted ethene cation radicals.

An ESR spectrum of (*E*)-1,2-bis(trimethylsilyl)ethene cation radical ($6^{+\cdot}$) showed a 38.1-G ($g = 2.0035$) triplet and was temperature independent. Interestingly, ESR spectra obtained from (*Z*)-1,2-bis(trimethylsilyl)ethene (**7**) showed a different feature from that of $6^{+\cdot}$. The ESR spectrum obtained from **7** was apparently a superposition of two triplets with the hfsc's of 54.8 and 36.0 G even at 96 K and very much temperature dependent. At the elevated temperatures, the outer triplet gradually disappeared with growing of the inner one. The hfsc of the latter triplet corresponds to that of $6^{+\cdot}$. Such a behavior is a strong indication that the two isomeric cation radicals have different structure and that smooth isomerization from $7^{+\cdot}$ to $6^{+\cdot}$ takes place even at temperature as low as 100 K. The larger hfsc of $7^{+\cdot}$ than that of $6^{+\cdot}$ suggests a larger twist angle of $7^{+\cdot}$ due to the significant steric strain between the two cis substituents in $7^{+\cdot}$.

An interesting deuterium isotope effect was observed in the olefinic ^{1}H hfsc of $8^{+\cdot}$ (34.0 G),[11] but the origin of the phenomenon remains still unclear. Further works are now in progress.

Acknowledgment. We thank Professor M. S. Gordon for his generous gift of an INDO program extended to second-row elements. Thanks are also due to Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

Registry No. 2, 5654-07-9; **3**, 17891-67-7; **4**, 26608-69-5; **5**, 18938-24-4; **6**, 18178-59-1; **7**, 18178-60-4; **8**, 87509-01-1.

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[4] Geometrical parameters other than a twist angle used for INDO calculation of $1^{+\cdot}$ were as follows: Bond lengths (Å) 1.11 (C–H² and C–H³), 1.12 (C–H¹), 1.40 (C–C), 1.48 (Si–H), and 1.85 (C–Si). Bond angles (deg) 109.5 (all C–Si–H and H–Si–H), 113.6 (H²–C–H³), 116.2 (H¹–C–C), 116.8 (H¹–C–Si), 122.9 (H²–C–H³), 123.5 (H³–C–C), and 127.0 (Si–C–C). An INDO program extended to second-row elements was kindly provided by Professor M. S. Gordon of North Dakota State University, cf.: Gordon, M. S.; Bjorke, M. D.; Marsh, F. J.; Korth, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 2670.

[5] $1\ G = 10^{-4}\ T$.

[6] Propene and fluoroethene cation radicals exhibited inverse dependence of the olefinic proton hfsc's on twist angles to $1^{+\cdot}$. Thus, a proton hfsc bound to the substituted olefinic carbon increases monotonously with increasing twist angles, while the residual olefinic proton hfsc's have a maximum. Such substituent dependence may suggest the major origin of the orbital interactions in twisted ethene cation radicals. This interesting problem will be discussed elsewhere in detail.

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[9] Hfsc and g values measured at 133 K are shown, except for those of $7^{+\cdot}$.

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[11] Deuterium hfsc was not well resolved. The best fit of the spectrum with the simulated was obtained when the hfsc was 6.1 G.