An ESR Study of a Tetrasilaspirobiindane Anion Radical. Stereoelectronic Electron-Accepting Effects of Trialkylsilyl Groups

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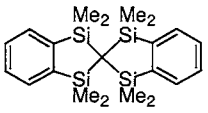
ESR spectra of a tetrasilaspirobiindane anion radical ($\mathbf{1}^-$) showed a doublet of doublet hfs pattern at low temperatures and significant line-width alternation, indicating that there is remarkable difference in the electron-accepting effects between two silyl substituents at the benzene ring with the unpaired electron due to the ring conformation.

Whereas a number of ESR studies of silyl-substituted benzene anion radicals have definitely shown the electron-accepting effects of the silyl substituents,[1] the stereoelectronic aspects have never been investigated by this technique. An ESR study of the anion radical of tetrasilaspirobiindane **1** ($\mathbf{1}^-$), in which two equivalent 1,2-disilylbenzenes are bound by a spirocarbon, has revealed that the unpaired electron is localized in a benzene ring but the spin distributing on the ring is remarkably different from that of 1,2-bis(trimethylsilyl)benzene **2** ($\mathbf{2}^-$). A doublet of doublet hfs pattern at low temperatures and line-width alternation of the ESR spectra of $\mathbf{1}^-$ indicate that the electronic effects of two silyl groups on the benzene ring with the unpaired electron are different from each other, due to the conformation of the two 1,3-disilacyclopentene rings. The results would be taken as the first experimental evidence for the hyperconjugative σ^* participation as the major reason for the electron-accepting ability of trialkylsilyl substituents rather than the d orbital participation.[2]



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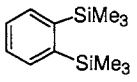

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Tetrasilaspirobiindane **1** was synthesized by a coupling reaction of 1,2-bis(chlorodimethylsilyl)benzene with carbon tetrachloride using magnesium in 28% yield as colorless crystals.[3] The molecular structure of **1** determined by X-ray crystallography is shown in Figure 1.[4] The 1,3-disilacyclopentene rings of **1** are not planar but have an envelope-like conformation, and therefore, two silyl groups attached to a benzene ring are not equivalent; the average bent angle of the envelop (angles between Si-C-C-Si and Si-C-Si planes) is 35°. However, the ^{1}H NMR spectrum of **1** at 154 – 303 K showed only three signals due to methyl protons on silicon and two-types of phenyl protons at δ 0.31, 7.35, and 7.53, indicating that the two silyl substituents on a benzene ring are averaged dynamically in solution through flip-flop processes among several ring conformations.

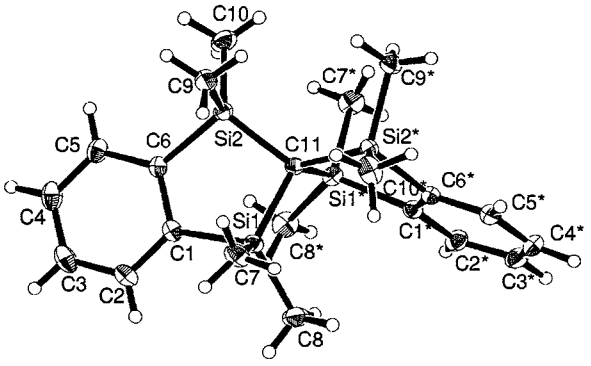


Figure 1. ORTEP drawing of tetrasilaspirobiindane **1** (30% probability): Selected bond lengths (Å): Si1–C1, 1.883(2); Si1–C7, 1.870(3); Si1–C11, 1.905(2). Selected bond angles (deg): C1–Si1–C7, 105.2(2); C1–Si1–C8, 114.7(1); C1–Si1–C11, 99.72(7); Si1–C11–Si2, 113.34(3).

Figure 2 shows ESR spectra of $\mathbf{1}^-$, which were generated by a short contact of **1** in 2-methyltetrahydrofurane (2-MeTHF) with potassium metal at –78 °C. The ESR spectrum at 293 K showed a 1:2:1 triplet with the hfs value of 0.54 mT. Since only two protons of $\mathbf{1}^-$ contribute to the splitting, it is concluded that the unpaired electron is localized in a benzene ring; there is neither significant spin delocalization over the whole molecule through spiro-conjugation nor facile electron transfer between the two benzene rings.[5] The splitting pattern and the hfs value of $\mathbf{1}^-$ at 253 K is similar to those of 1,2-bis(trimethylsilyl)benzene anion radical ($\mathbf{2}^-$), which shows a 1:2:1 triplet with the hfs value of 0.523 mT.[1b,f] The π spin distribution in $\mathbf{1}^-$ as well as $\mathbf{2}^-$ is calculated as 0.20 at C^4 and C^5 and almost zero at C^3 and C^6, using the McConnell equation, $a_H = Q\rho_C$, where $Q = 2.8$ mT;[6] the unpaired electron of $\mathbf{1}^-$ and $\mathbf{2}^-$ resides on the antisymmetric LUMO (π^*_A) of 1,2-disubstituted benzene.

The splitting pattern of $\mathbf{1}^-$ was remarkably temperature dependent as shown in Figure 2, while no significant change was observed in the ESR spectra of $\mathbf{2}^-$ between 153 and 233 K. At temperatures below 153 K, a doublet of doublet pattern of the spectrum was observed in $\mathbf{1}^-$ with the hfs values of 0.70 and

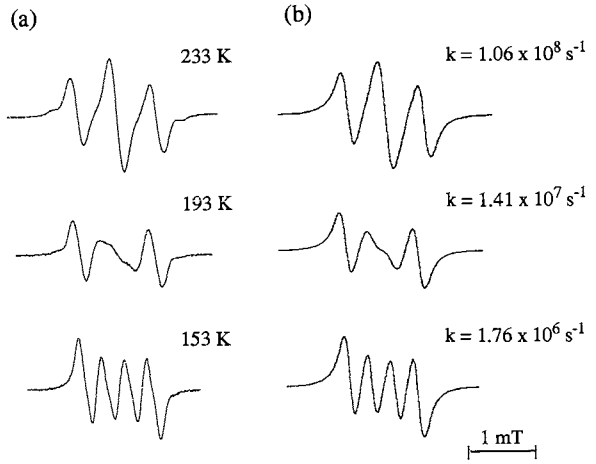


Figure 2. Temperature dependent ESR spectra of tetrasilaspirobiindane anion radical $\mathbf{1}^-$ in 2-MeTHF with potassium ion as a countercation: (a) experimental; (b) simulated with specified rate constants.

0.35 mT, which correspond to the spin densities of 0.250 and 0.125, at C^4 and C^5 (or C^5 and C^4), respectively. The nonequivalent spin densities at C^4 and C^5 will be caused by the different electron accepting ability of Si^1 and Si^2 at conformation **1A** in Figure 3. Actually, the π spin distribution was well reproduced by the HMO calculations using different parameters for the two silicon atoms.[7]

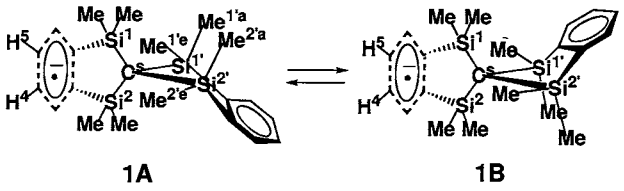
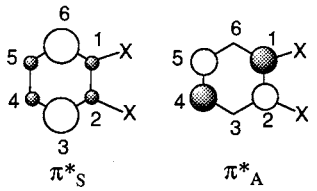
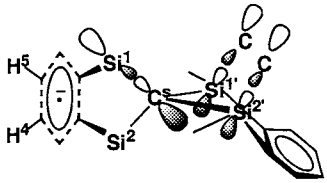


Figure 3. Ring flipping processes of 1^-.



Remarkable line-width alternation in the temperature range of 154 – 253 K will be explained in terms of the ring flipping process between **1A** and **1B** at higher temperatures. The exchange rates for the dynamic processes in $\mathbf{1}^-$ are determined by comparing the experimental spectra with the simulated spectra obtained by solving the modified Bloch equations for the two-jump system.[8] From a plot of ln(k/T) vs. 1/T, the following activation parameters were determined: $\Delta H^{\ddagger}$ = 3.3 kcal/mol and $\Delta S^{\ddagger}$ = 7.6 cal $mol^{-1}K^{-1}$).

The above results suggest that the electron accepting ability of the two silyl substituents at the anionic benzene ring in $\mathbf{1}^-$ is modified significantly by the arrangement of the alkyl-substituents on silicon atoms. An extra electron on a benzene ring is delocalized to σ*(Si^1-C^s) and σ*(Si^2-C^s) orbitals through the negative hyperconjugation, where C^s denotes the spiro carbon. Unequal electron-accepting ability between Si^1 and Si^2 moieties will be caused by the unequal interaction of the two σ* orbitals with the σ* orbitals in the other ring. Thus, at conformation **1A** in Figure 3, σ*(Si^1-C^s) orbital may have better overlap with σ*($Si^{1'}$-$Me^{1a'}$) and σ*($Si^{2'}$-$Me^{2a'}$) orbitals, in comparison to the overlap between σ*(Si^2-C^s) orbital and any σ* orbital on $Si^{1'}$ and $Si^{2'}$; in this case, the electron accepting ability of Si^1 will be larger than that of Si^2. Such remarkable stereoelectronic electron-accepting effects of a silyl-substituent are indicative of the hyperconjugative σ* participation rather than the d orbital participation as the major origin.[2]



The origin of the non-equivalence of two aromatic protons and the line-width alternation in the ESR spectra of $\mathbf{1}^-$ cannot be ascribed to the unsymmetrical ion pairing of $\mathbf{1}^-$ with the counter-cations, because similar phenomena were observed using various solvents and alkali metals.[9]

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References and Notes

1 a) J. A. Bedford, J. R. Bolton, A. Carrington, and A. R. H. Prince, *Trans Faraday Soc.*, **59**, 53 (1963). b) F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chim. Acta*, **51**, 707 (1968). c) H. Alt, E. R. Franke, and H. Bock, *Angew. Chem.* **81**, 538 (1969). d) F. Gerson, J. Heinzer, and H. Bock, *Mol. Phys.*, **18**, 461 (1970). e) H. Bock and W. Kaim, *Z. Anorg. Allg. Chem.*, **459**, 103 (1979). f) H. J. Sipe, Jr. and R. West, *J. Organomet. Chem.*, **70**, 353 (1974). g) H. J. Sipe, Jr. and R. West, *J. Organomet. Chem.*, **70**, 367 (1974).

2 For a recent discussion on electron-accepting effects of silyl substituents, see: Y. Apeloig, in "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley, New York (1989), Part 1, Chap. 2.

3 **1**: colorless crystals; mp 169–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 24 H), 7.35 (dd, J = 5.4 Hz, 3.3 Hz, 2 H), 7.53 (dd, J = 5.4 Hz, 3.3 Hz, 2 H); ^{29}Si NMR (59 MHz, $CDCl_3$) δ 5.4; ^{13}C NMR (75 MHz, $CDCl_3$) δ 3.0, 4.8, 128.2, 130.5, 151.1; MS (70 eV, EI) m/z 396 (M^+, 0.1), 381 (M^+-15, 100), 293 (25), 73 (70); HRMS found 396.1573, calcd for $C_{21}H_{32}Si_4$ 396.1581. *Anal.* Found: C, 63.72; H, 8.03%. Calcd for $C_{21}H_{32}Si_4$: C, 63.56; H, 8.13%.

4 Crystal data for **1**: $C_{21}Si_4H_{32}$; MW = 396.83; orthorhombic; a = 16.638 (4) Å, b = 8.427 (3) Å, c = 16.406 (4) Å; V = 2300.4 (9) $Å^3$; space group Pbcn; Z = 4; D_{calcd} = 1.146 g/cm^3. The final R and R_w factors were 0.036 and 0.037 for 2021 reflections with $F_o > 4\sigma(F_o)$.

5 A number of radical anions of spiro compounds having two perpendicular π systems have been investigated by ESR spectroscopy. Whether the spin delocalization occurs over the two π systems or not is dependent on the molecular structure and the generation conditions: R. D. Cowell and G. Urry, *J. Chem. Phys.*, **38**, 2028 (1963); F. Gerson, R. Gleiter, G. Moshuk, and A. S. Dreiding, *J. Am. Chem. Soc.*, **94**, 2919 (1972); F. Gerson, B. Kowert, and B. M. Peake, *J. Am. Chem. Soc.*, **96**, 118 (1974); H. Sakurai, T. Koyama, M. Kira, A. Hosomi, and Y. Nakadaira, *Tetrahedron Lett.*, **23**, 543 (1982); P. Maslak, M. P. Augustine, and J. D. Burkey, *J. Am. Chem. Soc.*, **112**, 5359 (1990); K. Ueda, M. Yamanoha, T. Sugimoto, H. Fujita, A. Ugawa, K. Yakushi, and K. Kano, *Chem. Lett.*, **1997**, 461.

6 H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

7 As studied by Bock et al.[1d] and West et al.,[1f] experimental π spin densities of silyl-substituted benzene anion radicals are well reproduced by HMO calculations. The spin densities at C^3 (C^6) and C^4 (C^5) of $\mathbf{2}^-$ are reproduced to be 0.187 and 0.003, respectively, using the following parameters: $\alpha_{Si} = \alpha - 2.0\,\beta$, $\beta_{C\text{-}Si} = 0.70\,\beta$, and $\alpha_C = \alpha - 0.20\beta$ at the silyl-substituted positions.[1f] If the $\beta_{C\text{-}Si}$ parameter for C^2–Si^2 overlap is reduced to 0.60β with the same values for the other parameters, the spin densities at C^4 and C^5 are modified to be 0.242 and 0.130, respectively, while they are 0.02 and 0.003 at C^3 and C^6; these values are good in accord with the experimental spin densities.

8 ESREXN program is used for simulation. Heinzer, J; QCPE No.209 (1972).

9 In the ESR spectra of $\mathbf{1}^-$•Rb^+ in 2-MeTHF, hyperfine splittings due to ^{85}Rb (I = 5/2, 72%) and ^{87}Rb (I = 3/2, 28%) were observed, while in DME there was no coupling interaction between $\mathbf{1}^-$ and Rb^+, indicating that $\mathbf{1}^-$ forms a solvent separated ion pair with Rb^+ in DME but a contact ion pair in 2-MeTHF. In both conditions, the line-width alternation due to the ring flipping process were observed in the temperature dependent ESR. The activation parameters for $\mathbf{1}^-$ with Rb^+ as the countercation are the following: $\Delta H^{\ddagger}$ = 4.6 and 3.5 kcal/mol and $\Delta S^{\ddagger}$ = 0.2 and 5.5 cal $mol^{-1}K^{-1}$, in 2-MeTHF and DME, respectively. The higher $\Delta H^{\ddagger}$ value in 2-MeTHF may be explained by the larger ion-pair interaction between the π anion radical and alkali metal ion.