CHEMISTRY LETTERS, pp. 1525-1528, 1985.

A BENT CYCLOPOLYSILANE ANION-RADICAL ($\underline{i}$-$Pr_2Si)_4$

Cynthia L. WADSWORTH, Robert WEST,* Yoichiro NAGAI,† Hamao WATANABE,†
Hideyuki MATSUMOTO,† and Tsutomu MURAOKA†

Department of Chemistry, University of Wisconsin, Madison, WI 53706, U.S.A.
†Department of Chemistry, Gunma University, Kiryu, Gunma 376

The ESR spectra for $(i\text{-}Pr_2Si)_4^{\overset{\cdot}{-}}$ and $(\underline{s}\text{-}Bu_2Si)_4^{\overset{\cdot}{-}}$ show two equally-intense splitting constants for α-^{13}C, indicating that these anion-radicals are bent and not rapidly interconverting.

Cyclopolysilanes undergo reduction to anion-radicals in which the unpaired electron is delocalized over the ring.$^{1)}$ Numerous anion-radicals of four-, five-, and six-membered ring cyclopolysilanes have been investigated by ESR spectroscopy in recent years.$^{2-8)}$ When these rings are of the form $(R_2Si)_n^{\overset{\cdot}{-}}$ (with all substituents R identical), in general they show only single values for the α-^{13}C hyperfine splitting constant (hfsc), as well as for the α-^{1}H hfsc when it is large enough to be observed. These findings imply that such anion-radicals $(R_2Si)_n^{\overset{\cdot}{-}}$, n = 4 to 6, are either planar or rapidly interconverting on the ESR time scale.

An exception to this generalization has now been observed, for octakis($\underline{i}$-propyl)cyclotetrasilane, $\underset{\sim}{1}$.$^{9)}$ The ESR spectrum for the anion-radical of $\underset{\sim}{1}$ in THF at -90 °C is shown in Fig. 1. Two equally-intense α-^{13}C sidebands are observed, with hfsc 18.58 and 14.40 G. Integration of the bands shows that each has an intensity corresponding to four carbon atoms. The spectrum indicates that anion-radical $(\underline{i}\text{-}Pr_2Si)_4^{\overset{\cdot}{-}}$ is nonplanar, and that interconvertion between equivalent nonplanar forms is slow compared to the ESR spin relaxation time. This interpretation is strengthened by the recent finding that the parent cyclosilane $\underset{\sim}{1}$ also exists in a folded, nonplanar conformation,$^{10)}$ with a ring bending angle of 37.1°.

The anion-radical of octakis($\underline{s}$-butyl)cyclotetrasilane, $\underset{\sim}{2}$,$^{9)}$ also shows

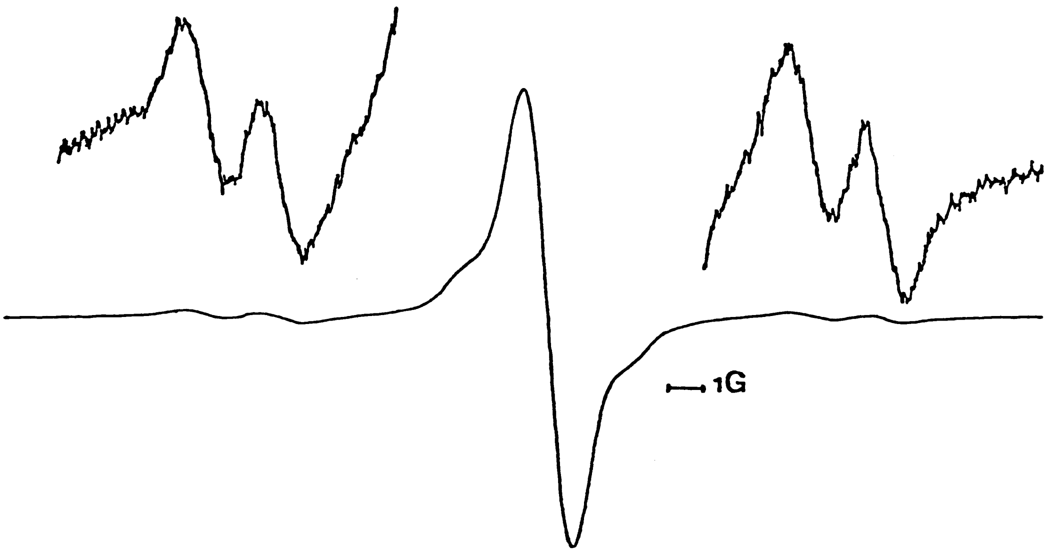

Fig. 1. ESR spectrum of $(\underline{i}\text{-Pr}_2\text{Si})_4^{\cdot-}$, electrochemically reduced, in THF at -90 °C. The inset spectra, determined at higher gain, show the equally-intense α-^{13}C sidebands.

two equally-intense α-^{13}C hfsc, Table 1. We interpret this finding as due to similar nonplanarity of the anion-radical; the structure of neutral **2** is as yet unknown but we predict that it will also be nonplanar. The ESR spectra of both compounds were temperature-independent over the range from -90 to -50 °C.

From these results it appears that the dichotomy between planar and nonplanar cyclotetrasilanes, recently discovered for neutral compounds, applies also to anion-radicals. The information available to date is listed in Table 1.

This work was supported in part by the U. S. Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. F49620-83-C-0044. The United States government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation thereon.

Table 1. Structures of Symmetrical Cyclotetrasilanes, as Neutral Molecules and Anion-Radicals

Neutral molecule				Anion-radical		
R in $(R_2Si)_4$	Structure	Dihedral angle/deg	Ref.	α-^{13}C,G	Structure	Ref.
Me	planar	0	11	20.97	p-r$^{a)}$	7
Et				18.40	p-r$^{a)}$	7
Me_3Si	planar	0	12			
Ph	bent		13	13.1	p-r$^{a)}$	3,8
i-Pr	bent	37.1	10	18.58, 14.40	bent	this work
s-Bu				18.36, 14.42	bent	this work
Me_3SiCH_2	bent	38.8	10,14			
Me_3CCH_2	bent	38.8	15			

a) Either planar or rapidly interconverting.

References

1) For a review see R. West, Pure Appl. Chem., 5, 1041 (1982).

2) E. Carberry, R. West, and G. E. Glass, J. Am. Chem. Soc., 91, 5446 (1969).

3) M. Kira and H. Bock, J. Organomet. Chem., 164, 277 (1979).

4) B. J. Helmer and R. West, Organometallics, 1, 1458 (1982).

5) R. West and E. S. Kean, J. Organomet. Chem., 96, 323 (1975); A. C. Buchanan and R. West, ibid., 172, 273 (1979).

6) B. Kirste, R. West, and H. Kurreck, J. Am. Chem. Soc., 107, 3013 (1985).

7) C. L. Wadsworth, R. West, Y. Nagai, H. Watanabe, and T. Muraoka, Organometallics, in press.

8) C. L. Wadsworth and R. West, Organometallics, in press.

9) H. Watanabe, T. Muraoka, M. Kageyama, and Y. Nagai, J. Organomet. Chem., 216,

C45 (1981); H. Watanabe, T. Muraoka, M. Kageyama, K. Yoshizumi, and Y. Nagai, Organometallics, 3, 141 (1984).

10) H. Watanabe and Y. Nagai, "Organosilicon and Bioorganosilicon Chemistry," ed by H. Sakurai, Ellis Horwood Limited, Chichester, West Sussex, England (1985), Chap. 9, pp.107-114; H. Watanabe, M. Kato, T. Okawa, Y. Kougo, Y. Nagai, and M. Goto, Organometallics, submitted.

11) C. Kratky, H. G. Schuster, and E. Hengge, J. Organomet. Chem., 247, 253 (1983).

12) Y.-S. Chen and P. Gaspar, Organometallics, 1, 1410 (1982).

13) L. Parkanyi, K. Sasvari, and I. Barta, Acta Crystallogr., Sect.B, 34, 883 (1978).

14) H. Watanabe, Y. Kougo, M. Kato, H. Kuwabara, T. Okawa, and Y. Nagai, Bull. Chem. Soc. Jpn., 57, 3017 (1984).

15) H. Matsumoto, M. Minemura, K. Takatsuna, Y. Nagai, and M. Goto, Chem. Lett., in press.

(Received July 20, 1985)