iodination.[12,13] No definite information is available as to the remaining two residues. From our data it appears likely that residues 92 and 115 contribute to the aromatic Cotton effect.

(12) C.-Y. Cha and H. A. Scheraga, *J. Biol. Chem.*, **238**, 2965 (1963).
(13) L. G. Donovan, *Biochim. Biophys. Acta*, **78**, 473 (1963).

Alexander N. Glazer
Department of Biological Chemistry, Center for the Health Sciences
University of California, Los Angeles, California 90024

Norman S. Simmons
Department of Biophysics and Nuclear Medicine
Laboratory of Nuclear Medicine and Radiation Biology
Center for the Health Sciences
University of California, Los Angeles, California 90024

Figure 1. E.s.r. spectrum of radical anion at low gain, showing relative intensity of central lines.

The Radical Anion of Dodecamethylcyclohexasilane[1]

Sir:

Radical anions are well known in which unpaired electrons occupy low-lying antibonding π molecular orbitals,[2] but only recently have radical anions of saturated systems (cyclopropane[3] and adamantane[4]) been reported. These latter discoveries prompted us to investigate the possibilities of radical-anion formation from alkylpolysilanes, wherein low-lying d orbitals might play an important role in accepting an electron. This communication reports the reduction of dodecamethylcyclohexasilane to give a paramagnetic species. The electron spin resonance spectrum of the species suggests that it is the anion radical of the parent cyclosilane, $[Si(CH_3)_2]_6{}^{-}$, in which the unpaired electron is delocalized over all six silicon atoms.

Reaction of a solution of dodecamethylcyclohexasilane in the mixed solvents tetrahydrofuran-1,2-dimethoxyethane (2:1) with sodium–potassium alloy at $-95°$ results in a blue-green solution which exhibits strong electron paramagnetic resonance. The spectrum becomes fully resolved upon warming to $-75°$. At low gain (Figure 1) it consists of about 19 equally spaced lines, with spacing 0.53 gauss and line width 0.11 gauss, centered at $g = 2.0032$. The relative intensities of the 13 central lines are 11:14:39:53:80:95:100:95:79:56: 35:12:9, corresponding fairly well to the intensities expected for the central lines of a 37-line distribution, which would be expected if the unpaired electron interacted equally with all 36 protons.

At higher gain about 25 of the expected 37 lines can be observed (Figure 2), but the pattern is complicated by the presence of two satellite spectra which appear to replicate the principal spectrum. The first has an intensity of about 5% of the main spectrum and corresponds to a doublet with a splitting of 15.8 gauss. Each half of the doublet contains at least 13 lines ($a = 0.53$ gauss, line width $= 0.11$ gauss). The second, also a doublet, has an intensity about 12% of that of the main spectrum. It contains at least 11 lines in

(1) This research was supported by a contract from the Atomic Energy Commission and a grant from the Air Force Office of Scientific Research.
(2) For reviews see E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1965); A. Carrington, *Quart. Rev.* (London), **17**, 67 (1963).
(3) K. W. Bowers and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 2331 (1963).
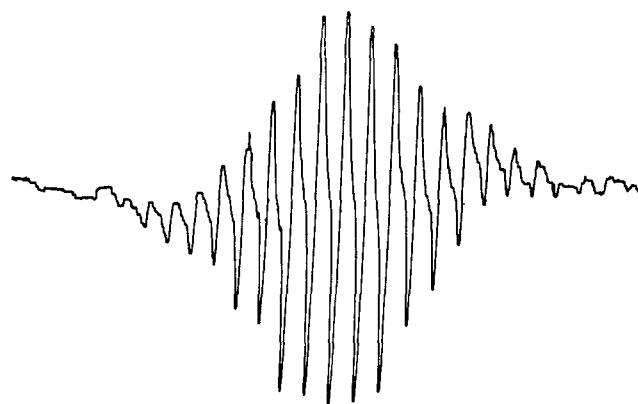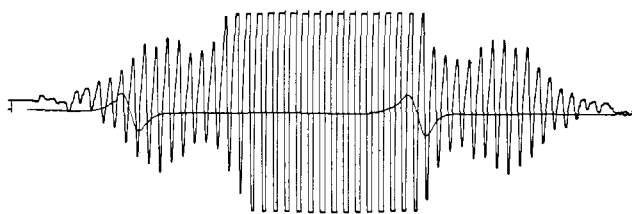(4) K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *ibid.*, **85**, 3707 (1963).

Figure 2. E.s.r. spectrum of radical anion at high gain, showing satellite spectrum with splitting 15.8 gauss attributed to [13]C. The spectrum of peroxylamine disulfonate anion in water, recorded simultaneously (double cavity), is superimposed for calibration.

each half, also with $a = 0.53$ gauss and line width 0.11 gauss. Because of the small hyperfine splitting of 5.25 gauss, the second satellite is almost superimposed on the main resonance lines. Within each satellite cluster, the relative line intensities correspond roughly to the binomial distribution for $n = 36$ mentioned above.

The two doublets are not due to interaction with an alkali metal,[5] for the spectrum is identical when the anion radical is prepared using pure sodium or pure potassium instead of a mixture of the two metals. Tentatively, the satellites are assigned to splitting by carbon-13 and silicon-29. In the system under consideration these isotopes should produce doublet satellite patterns with relative intensities of 6.7 and 14.2% of the main spectrum, respectively, if delocalization is complete.

The observed e.s.r. spectrum suggests that the unpaired electron is delocalized equally over all six silicon atoms and so contacts equally all of the protons on the twelve methyl groups of the molecule. If this interpretation is correct, the unpaired electron must reside in a π- (or δ-) type orbital made up of 3d orbitals from the six silicon atoms.[6] In this model, because d-orbital combinations are considered, the six silicon atoms do not necessarily have to be coplanar for effective delocalization over the ring. However, ring interconversion is required to make all of the methyl groups equivalent on a time-average basis.

The e.s.r. signal was observed with undiminished intensity up to about $-50°$. Above this temperature the signal disappears rapidly and the solution becomes

(5) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958).
(6) We believe that similar orbitals may be involved in electronic excitation of polysilanes. See H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.* (Amsterdam), **2**, 369 (1964).

pale yellow in color. Dodecamethylcyclohexasilane can be converted to its anion radical in the presence of an excess of benzene, which indicates that the cyclosilane has a higher electron affinity than benzene.

Preliminary attempts have been made to form anion radicals from other permethylated polysilanes. Hexamethyldisilane gave no radical signal after repeated attempts at reduction, but linear decamethyltetrasilane gave complex e.s.r. spectra under the conditions described above. Attempts to rationalize these spectra are under way, and extensions to related organometallic systems are planned.

G. Ronald Husk, Robert West

Department of Chemistry, University of Wisconsin
Madison, Wisconsin

The Dependence of Directly Bonded Coupling Constants upon the Effective Nuclear Charge

Sir:

The practice of relating directly bonded carbon-13 proton coupling constants with per cent "s" character in the C–H bond is receiving such general acceptance that a critical evaluation is needed of other factors important in this experimental parameter. The hybridization criterion is based on theoretical considerations[1,2] and on observed empirical relationships.[3–5] Additive substituent effects[6] upon $^{(1)}J_{C_{13}-H}$ have been attributed[7] also to variations in the bond hybridization.

The importance of factors other than the "s" character of a C–H bond is portrayed in eq. 1, which is

$$^{(1)}J(K) \cong \left(\frac{\Delta_{CH_4}}{\Delta_K}\right)\left(\frac{N_K}{N_{CH_4}}\right)^2\left(\frac{\alpha_K}{\alpha_{CH_4}}\right)^2\left(\frac{Z_K}{Z_{CH_4}}\right)^3 {}^{(1)}J(CH_4) \quad (1)$$

obtained directly from eq. 4 of Karplus and Grant,[1] where $^{(1)}J(K)$ is the coupling constant in the Kth bond of a substituted methane, $^{(1)}J(CH_4)$ is 125 c.p.s., Δ is the average excitation energy which should not vary greatly for various C–H bonds, N is the bond normalization constant defined previously,[1] α^2 is a parameter which is directly proportional to the "s" character, and Z represents the effective nuclear charge appearing in the radial function of a carbon 2s orbital of the form $(Z_K/a_0)^{3/2}\{A + B(Z_K/a_0)r\} \exp(Z_K r/2a_0)$. It is apparent from eq. 1 that neglect of minor changes in Z, which is raised to the third power as also noted by Shoolery,[3] will invalidate conclusions regarding bond hybridization.

As a means of estimating variations in Z_K, it is useful to consider the charge transfer, Q_K, defined by eq. 2

$$Q_K = \frac{2\lambda_K S_K + \lambda_K^2}{2 + 2S_K^2 + 4\lambda_K S_K + \lambda_K^2} \quad (2)$$

for the $u_K(i,j)$ bond orbital (see ref. 1), where the bond overlap is S_K, and λ_K is the corresponding ionic coefficient. Q_K is positive for an electron shift toward the

(1) M. Karplus and D. M. Grant, Proc. Natl. Acad. Sci. U. S., 45, 1269 (1959).
(2) C. Juan and H. S. Gutowsky, J. Chem. Phys., 37, 2198 (1962).
(3) J. N. Shoolery, ibid., 31, 1427 (1959).
(4) N. Muller and D. E. Pritchard, ibid., 31, 768, 1471 (1959).
(5) N. Muller, ibid., 36, 359 (1962).
(6) E. R. Malinowski, J. Am. Chem. Soc., 83, 4479 (1961).
(7) H. S. Gutowsky and C. S. Juan, ibid., 84, 307 (1962).

carbon atom. Application of Slater screening concepts in eq. 3 relates Z_K to Q_K. The summation is over

$$Z_K = Z_0 - S \sum_K{}' Q_K \quad (3)$$

all bonds centered on the carbon-13 except the C–H bond giving rise to the spin–spin splitting. S is the Slater screening parameter (0.35) and Z_0 is a reference bond effective nuclear charge. Coulson[8] has suggested that $Z_{CH_4} = 3.25\beta$ where $\beta = 1.1$–1.2. Using $\beta = 1.15$, it was found that the value of Q_{CH} which gave the best fit for all of the experimental data in Table I was 0.18,[9] and a value of 3.929 was obtained for Z_0. The normalization constant, N_K, follows directly from λ_K and S_K, which are specified by eq. 2.

Table I

Compound	$(N_K/N_{CH_4})^2$	$(Z_K/Z_{CH_4})^3$	— $^{(1)}J_{CH}$, c.p.s. — Calcd.	Exptl.	Difference
CH₄	1	1	[125]	125[a]	0
CH₃F	1.033	1.213	156.7	149[a]	7.7
CH₃Cl	1.028	1.181	151.8	151[d]	0.8
CH₃Br	1.025	1.166	149.4	151.0[c]	−1.6
CH₃I	1.021	1.141	145.6	150.5[c]	−4.9
CH₃–O–	1.021	1.138	145.2	140–147[f]	−1.8 to +5.2
CH₂F₂	1.070	1.454	194.5	185[h]	9.5
CH₂Cl₂	1.060	1.383	183.3	178[a]	5.3
CH₂ClBr	1.057	1.366	180.5	179.5[c]	1.0
CH₂Br₂	1.055	1.349	177.8	178[e]	−0.2
CH₂I₂	1.046	1.294	169.3	173[a]	−3.7
CH₂(OCH₃)₂	1.045	1.288	168.3	162[b]	6.3
CHF₃	1.106	1.725	238.5	238[b]	0.5
CHF₂Cl	1.101	1.685	231.9	231[b]	0.9
CHCl₂F	1.096	1.646	225.5	220[b]	5.5
CHCl₃	1.091	1.607	219.1	209[a]	10.1
CHBr₃	1.084	1.550	209.9	206[a]	3.9
CHI₃	1.071	1.461	195.7	. . .[g]	
CH(OCH₃)₃	1.070	1.450	193.9	186[b]	7.9

[a] See ref. 4. [b] N. Muller and P. I. Rose, J. Am. Chem. Soc., 84, 3973 (1962). [c] G. S. Reddy and J. H. Goldstein, J. Chem. Phys., 38, 2736 (1963). [d] H. Spiesecke and W. G. Schneider, ibid., 35, 722 (1961). [e] See ref. 6. [f] (CH₃)₂O, 140[b]; CH₃OH, 141[a]; CH₃-OC₆H₅, 143[a]; p-CH₃OC₆H₄CHO, 145[a]; (CH₃O₂CCH₂)₂, 147.[a] [g] Not available. [h] See ref. 5.

Values of Q_K for a carbon–halogen bond are estimated with bond dipole moments from Moelwyn-Hughes[10] from the proportional relationship $(\mu_K R_{CH}/\mu_{CH} R_K)Q_{CH}$, where μ_K and R_K are the bond dipole moment and bond distance, respectively, of the Kth bond. These Q_K values then are used to obtain λ_K, S_K, N_K, and Z_K. While relatively small changes in Z_K are realized for the degree of bond polarization assumed here, significant effects on $^{(1)}J(K)$ result from this third-power correction as observed in Table I for the various halogenated methanes. For the purposes of this treatment, the ratios Δ_{CH_4}/Δ_K and $(\alpha_K/\alpha_{CH_4})^2$ are assumed to be unity in the predicted values given in Table I.

The agreement between calculated and experimental coupling constants may be improved by the inclusion of Δ and α^2. It is shown, however, that reasonable changes in the effective nuclear charge can account for

(8) C. A. Coulson, Trans. Faraday Soc., 38, 433 (1942).
(9) A. value of 0.33 is required to fit a C–H bond dipole moment of 0.4 D. (see ref. 8). Coulson has indicated, however, that a 0.33 value is probably too large.
(10) E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd Revised Ed., Pergamon Press, New York, N. Y., 1961, p. 530.