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ELECTRON SPIN RESONANCE STUDIES OF GROUP IV ORGANOMETALLIC RADICAL ANIONS

I. ORGANOMETAL-SUBSTITUTED BENZENES

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Summary

Electron spin resonance spectra have been measured under uniform conditions for a series of trimethylsilyl-substituted benzene anion radicals. These ESR results have been used to derive a general set of Hückel molecular orbital parameters by treating the organosilyl substituent as a pseudo-heteroatom. ESR data for radical anions of organosilyl-substituted benzenes, biphenyls and naphthalenes are reproduced accurately by MO calculations employing $h_{Si} = -2.0$ and $k_{CSi} = 0.7$. For these series of compounds, the silicon-methyl proton ESR splittings, while not related to the π electron density on silicon alone or to the density on the aromatic carbon to which silicon is bonded, may be related to a combination of the π spin densities by a semiempirical relation:

$$a^{H}_{SiCH_3} = \rho_{C'} Q^{H}_{C'SiCH_3} + \rho_{Si} Q^{H}_{SiCH_3}$$

with $Q^{H}_{C'SiCH_3} = 1.90$ and $Q^{H}_{SiCH_3} = -2.35$ gauss.

Introduction

Dative π-bonding effects frequently are invoked as explanations of certain properties of the organometal compounds of Group IVA [1]. In addition to the classical studies cited in ref. 1, newer physical techniques have been applied to investigate bonding in organosilicon compounds. In particular, Bock and coworkers have investigated the placement of molecular energy levels in organosilicon compounds by UV spectroscopy [2], by determining UV spectra of charge transfer complexes [2, 3], and by photoelectron spectroscopic measurements [4]. A consistent picture of R_3Si substituents as $+I$ σ electron donors and as relatively weak $-R$ π-electron acceptors emerges. Schweig's photoelectron spectroscopic (PES) studies of vinylsilanes also provide support for interaction (through conjugation) between adjacent π-electron systems connected by silicon [5]. However, the dangers inherent in the assignment of PES bands, aptly described by

Heilbronner et al [6] may justify scepticism concerning the application of Koopman's Theorem to electronic systems with localized charge densities.

Recent determinations of substituent chemical shifts for ^{19}F NMR resonances also suggest that R_3Si groups participate in $d_\pi{-}p_\pi$ electron withdrawal in F—Aromatic—SiR_3 systems [7—9]. In contrast, investigations of N—Si interactions by ^{15}N NMR spectroscopy produced results that could be explained without the use of a π-bonding model [10, 11].

Electron spin resonance (ESR) studies of organometal-substituted radical anions provide strong evidence for these $d_\pi \leftarrow p_\pi$ interactions [12]. The evidence is of several forms: (1) Hyperfine splitting (hfs) from silyl-methyl protons in $Me_3SiC_6H_5$ radical anion suggests that the molecular orbital of the unpaired electron extends to the silicon atom [13]. (2) ESR spectra of $Me_3MC_6H_5$ anions indicate that the Me_3M-substituent is electron attracting for M = Si, Ge but is electron releasing for M = C [13]. (3) Hückel and Hückel—McLachlan molecular orbital calculations for organometal-substituted biphenyls, based on models treating the metal as a pseudo-heteroatom and producing agreement of calculated and experimental spin densities, predict significant carbon—metal π-bond orders [14, 15]. (4) Hammett σ^- constants, determined by ESR studies of organometal-substituted semidione anions, indicate that Me_3Si and Me_3Ge are moderately good electron-withdrawing groups [16, 17].

We wish to report the results of ESR investigations that confirm ESR data reported earlier by independent workers [18, 19]. Our data, measured under uniform experimental conditions, have permitted the determination of general molecular orbital parameters for R_3M substituents (M = Si, Ge) on aromatic systems. These parameters have been used in a tentative investigation of the mechanism of ESR hyperfine splitting by silyl-methyl protons.

Experimental

Materials. Trimethylsilylbenzene and pentamethyldisilanylbenzene were prepared by standard procedures and purified by gas chromatography; their infrared spectra were identical with authentic samples. Tris(trimethylsilyl)silylbenzene was donated by Prof. Henry Gilman. After a gas chromatography purity check, it was used as received. *Meta-* and *para-*bis(trimethylsilyl)benzene were prepared by mixing the corresponding dibromobenzene with excess lithium metal in the presence of excess trimethylchlorosilane. The reactions were carried out in anhydrous tetrahydrofuran in an argon atmosphere. Identity of the products was established by infrared spectroscopy [20].

Electron spin resonance spectra. First derivative ESR spectra were determined using a Varian V-4502-13 X-band spectrometer with 100 kHz field modulation and equipped with a Varian V-4532 dual cavity. Sample temperature was regulated with a Varian V-4540 variable temperature accessory and insert Dewar.

The solvent used was a 2/1 mixture of 2-methyltetrahydrofuran and 1,2-dimethoxyethane. Reductions of the organometal-substituted benzenes were carried out with sodium—potassium alloy, in a toluene slush bath at —95° C. The details of the experimental procedures have been published [21—23]. Spectra were normally recorded at —70° to —80°. Experiments between —50° and

—100° showed that the hyperfine splitting constants have little temperature dependence.

Results and discussion

ESR results. Hyperfine coupling constants and g values for radical anions of organosilyl-substituted benzenes are presented in Table 1. Carrington's ESR studies of trimethylsilylbenzene anion indicate that trimethylsilyl slightly perturbs the molecular orbitals of benzene [13]. The molecular orbitals for aromatic compounds with weakly perturbing substituents may be described approximately by the orbitals of the parent aromatic molecule [13, 24]. In benzene radical anion, the unpaired electron is in an orbital that is a mixture of the two lowest unfilled degenerate orbitals, the antisymmetric (A) and symmetric (S). However, if the benzene ring is substituted, the degeneracy of A and S is removed, and the unpaired electron may be considered to occupy either A or S*. Substitution on benzene will leave A unchanged in energy, but S will be raised or lowered depending on whether the substituent is electron releasing or electron withdrawing, respectively (Fig. 1). Since ESR hyperfine splittings are proportional to unpaired electron density, one expects large ring proton splittings if A is lower (and hence occupied) and, conversely, small hfs from *ortho* and *meta* protons plus large hfs from the *para* proton if S is lower. A simple extension of this argument predicts that S will be occupied in *para*-disubstituted benzene anions and A in *meta*-disubstituted benzene anions if the substituents are electron withdrawing.

The observed hyperfine splitting constants are listed in Table 1, and typical spectra are shown in Figs. 2 and 3. The form of all of the ESR spectra follows from the qualitative molecular orbital arguments given above, assuming that the

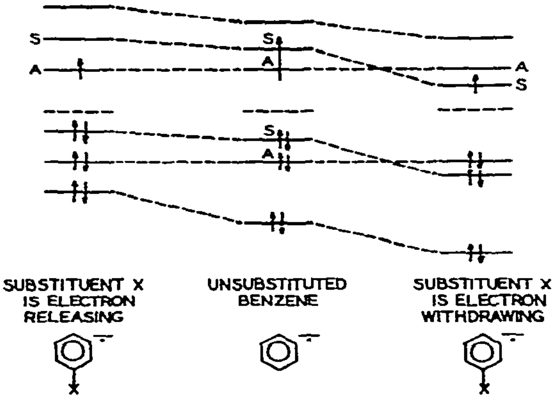

Fig. 1. Removal of A—S degeneracy upon substitution of benzene by weakly perturbing group, X.

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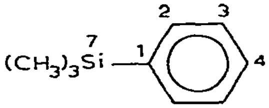
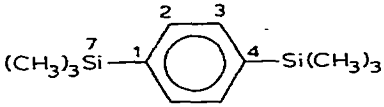
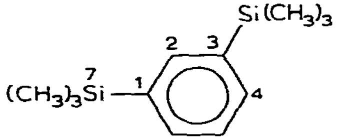
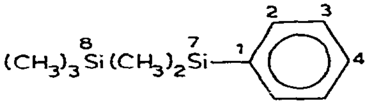
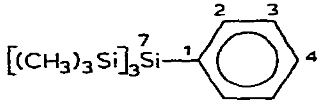
*In higher order approximations, the exact form of the wavefunctions describing A and S are altered slightly by substituent perturbations of A and S and by vibronic mixing, but consideration of these effects does not impair the qualitative argument given here. See ref. 25.

TABLE 1

ESR RESULTS FOR ANION RADICALS OF ORGANOSILYL-SUBSTITUTED BENZENES

Compound	g^a	a_2^b	a_3	a_4	a_{SiCH_3}	
	2.0028	2.66 (2.65)	1.06 (1.06)	8.18 (8.09)	0.26 (0.26)	
	2.0028	1.77 (1.76)	1.78 (1.76)	— —	0.27 (0.27)	
	2.0028	0.24 (0.23)	— —	6.98 (6.94)	0.24 (0.17)	a_5 0.72 (0.83)
	2.0028	2.66 (2.67)	0.95 (0.93)	8.09 (8.15)	0.14^c (—)	
	2.0028	2.89	1.03	7.84	—	

[a] g-values were measured by the dual-cavity technique at −100°C using Fremy's salt as the reference; they are believed accurate to ±0.0001. [b] Hyperfine coupling constants are reported in gauss and are believed accurate to ±0.05. Values in parentheses are independent results reported in ref. 18. [c] Silicon-methyl hyperfine splitting measured peak-to-peak from incompletely resolved spectrum.

trialkylsilyl substituents are electron withdrawing. Trimethylsilylbenzene, pentamethyldisilanylbenzene and tris(trimethylsilyl)silylbenzene anions (Fig. 2) all have large doublet hfs from the ring *para* proton; hfs by two *ortho* and two *meta* protons produces a triplet-of-triplets superimposed on the original doublet, and silyl-methyl proton hfs is observed as fine structure on the ring proton hfs. ESR spectra of *p*- and *m*-bis(trimethylsilyl)benzene (Fig. 2) are consistent with those expected for occupation of the S and A molecular orbitals, respectively.

Molecular orbital calculations. In view of the success of the qualitative MO considerations in interpreting all the experimental data, we have chosen the simple theoretical model of Hückel MO theory with pseudoheteroatom metal atoms. More sophisticated models have been developed [26] and applied to ESR results for trimethylsilyl-substituted anilines [27]. The molecular orbital treatment of organometal-substituted benzenes must provide calculated spin densities that agree with experimental spin densities obtained from experimental hyperfine coupling constants (hfcc) and McConnell's relation [28]: $a_i = Q\rho_i$. The param-

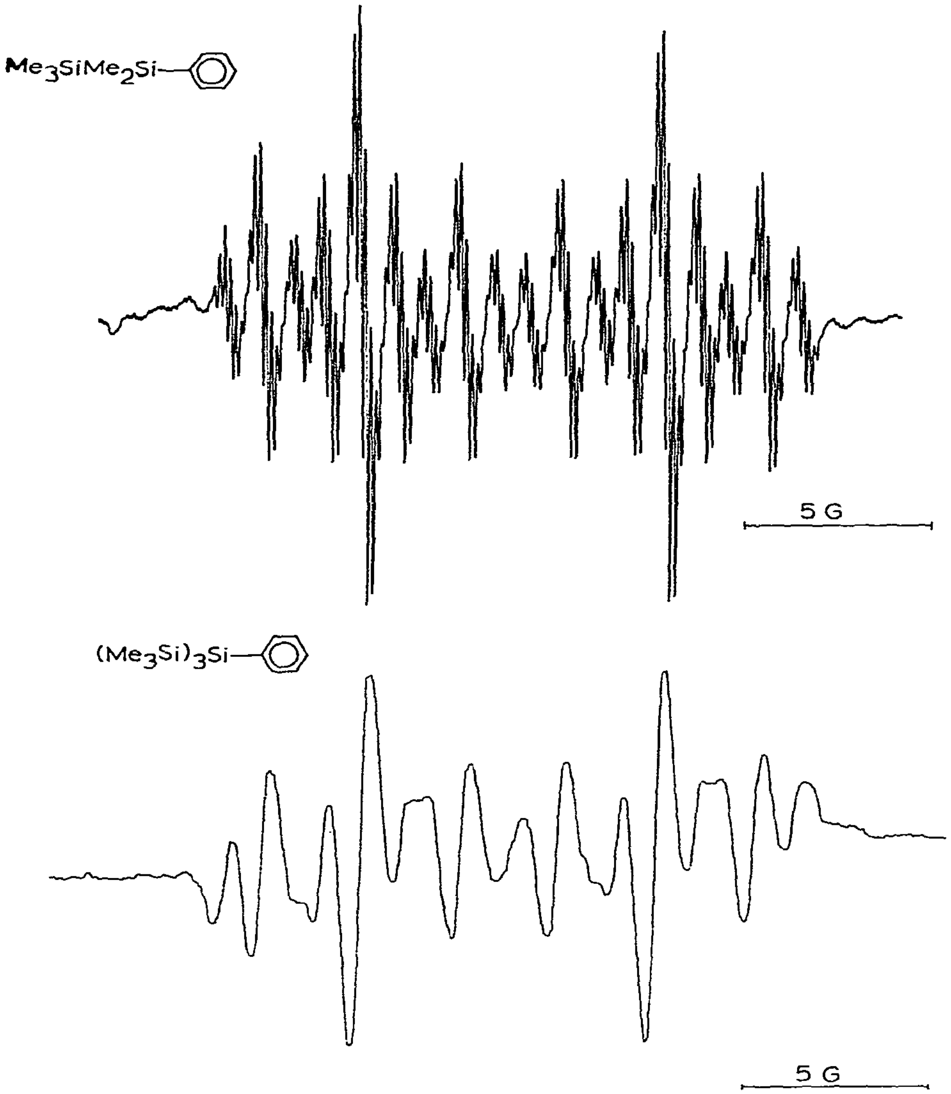


Fig. 2. (Above) ESR spectrum of pentamethyldisilanylbenzene radical anion, −60°; (below) ESR spectrum of tris(trimethylsilyl)silylbenzene radical anion, −100°.

eters of the relation have their usual significance; in the present work, the value of −28.0 gauss was adopted for Q [29]. If the unpaired electron occupies molecular orbital j, then the unpaired electron density at atom i is $\rho_i = c_{ij}^2$ where c_{ij} is the coefficient of the $2p_z$ atomic orbital in the Hückel LCAO-MO: $\Psi_j = \Sigma c_{ij}(2p_{zi})$. The c_{ij} were calculated by either the Hückel [30] or Hückel-McLachlan [31] procedures. Organometal-substituents were considered to be heteroatoms in the aromatic π-electron system [14, 32]. Coulomb and resonance in-

Fig. 3. ESR spectra of *m*-bis(trimethylsilyl)benzene radical anion: low resolution (top) −100° and high resolution (bottom) −100°.

tegrals for a heteroatom were scaled in terms of the resonance integral of an ordinary aromatic carbon—carbon bond:

$\alpha_M = \alpha_C + h_M \beta_{CC}$ $\qquad$ $\beta_{CM} = k_{CM} \beta_{CC}$

The inductive effect of metal substituents was incorporated in the calculation by use of an auxiliary inductive parameter, δ, usually assigned the value 0.10: $\alpha_{C'} = \alpha_C + h_M \delta_{CC}$, where C′ is the aromatic carbon bearing the organometal substituent.

TABLE 2

HÜCKEL AND HÜCKEL—McLACHLAN PARAMETERS FOR TRIMETHYLSILYL- AND TRIMETHYLGERMYL-SUBSTITUENTS

Substituent	Hückel	Hückel—McLachlan
Me_3Si	$h_{Si} = -2.00$ $k_{CSi} = 0.70$	$h_{Si} = -1.80$ $k_{CSi} = 0.70$ λ 0.30
Me_3Ge	$h_{Ge} = -1.45$ $k_{CGe} = 0.40$	$h_{Ge} = -1.40$ $k_{CGe} = 0.40$ λ 0.10

Heteroatom parameters h_M and k_{CM} were treated as adjustable parameters in Hückel and Hückel—McLachlan molecular orbital calculations. Dependence of spin densities at ring carbon atoms of $M-C_6H_5$ was investigated for the ranges $-0.8 \leqslant h_M \leqslant -3.0$ and $0.2 \leqslant k_{CM} \leqslant 1.0$. Best agreement of calculated and experimental spin densities, and ratios of spin densities, occurred with the heteroatom parameters reported in Table 2. Both molecular orbital treatments produced good agreement between calculated and experimental densities, but the McLachlan method was better for positions with small densities. Previous investigators who derived heteroatom parameters for Me_3Si and Me_3Ge substituents on biphenyl and naphthalene, reported difficulties in applying McLachlan's procedure to their molecules [14]. In accordance with Nowakowski [33], we find that variation of McLachlan's λ parameter produced spin densities in agreement with experimental ones. The generality of the heteroatom parameters is evident from the molecular orbital calculations of Table 3 for organometal-substituted benzenes, biphenyls and naphthalenes.

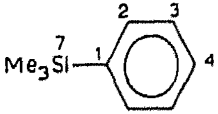
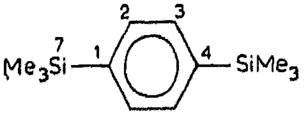
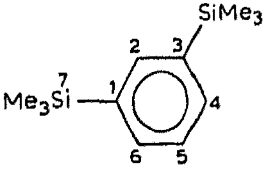
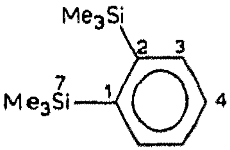
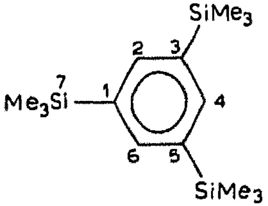
π-Electron charge densities of 0.04 and 0.02 are predicted for Si and Ge of uncharged $Me_3M-C_6H_5$. The corresponding metal—carbon bond π-orders, 0.21 (Si—C) and 0.14 (Ge—C), are slightly larger than those calculated by Allred and coworkers for analogous organometal-substituted biphenyls [14, 15].

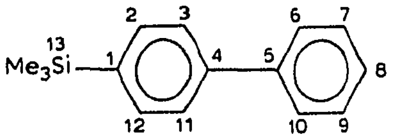
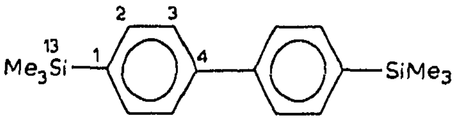
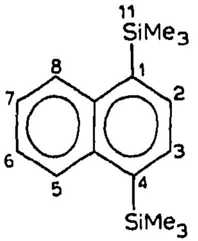
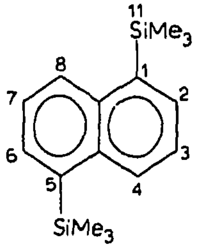
Silylmethyl proton hyperfine interaction. Examination of Table 3 indicates only a general trend in silyl-methyl proton hyperfine splittings: they tend to be larger in molecules where calculations predict large spin densities on the silicon atom and on the adjacent aromatic carbon atom. Janzen and coworkers have suggested a semiempirical relation of the form $a^H_{SiCH_3} = \rho_{Si}Q^H_{SiCH_3}$ with $Q^H_{SiCH_3} = 1.0$ for the anion radical of 1,4-disilacyclohexadiene and related compounds [34]. Assuming that our molecular orbital calculations (which faithfully reproduce proton hyperfine splittings) adequately predict spin densities in the molecules of Table 3, no relation similar to Janzen's holds for these molecules. Nor does the following relation adequately predict silyl-methyl proton hyperfine splittings: $a^H_{SiCH_3} = \rho_{C'}Q^H_{C'SiCH_3}$. By analogy with the work of McLachlan [35] on substituent methyl groups and of Karplus and Fraenkel [36] on carbon-13 hyperfine splittings, we developed an empirical, two-term relationship including a contribution from spin density on the carbon (C′) to which Me_3Si is substituted as well as from spin density on the silicon of Me_3Si. Least squares treatment of the available data gives: $a^H_{SiCH_3} = 1.90\ \rho_{C'} - 2.35\ \rho_{Si}$. This relation fits the experimental silyl-methyl proton hyperfine splittings for all of the eight

(continued on p. 364)

TABLE 2

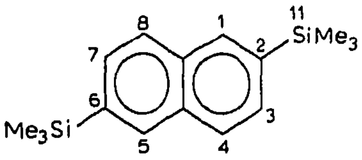
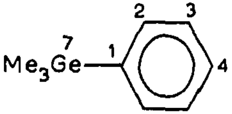
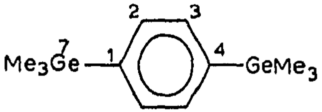
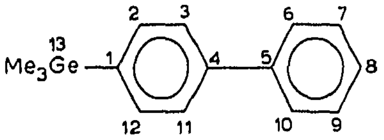
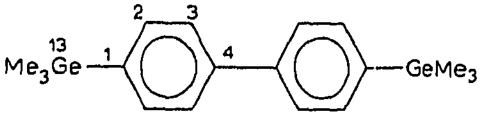
COMPARISON OF EXPERIMENTAL AND CALCULATED SPIN DENSITIES IN ORGANOMETAL-SUBSTITUTED RADICAL ANIONS

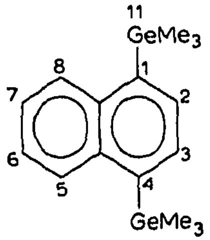
Compound	Position	a_{expt}[a]	ρ_{expt}[b]	ρ_{HMO}[c]	ρ_{Mac}[d]
	1	—	—	0.282	0.276
	2	2.66	0.095	0.096	0.098
	3	1.06	0.038	0.060	0.040
	4	8.18	0.292	0.287	0.294
	7	0.24	—	0.118	0.154
	1	—	—	0.256	0.251
	2	1.78	0.064	0.074	0.066
	7	0.27	—	0.095	0.116
	1	—	—	0.188	0.173
	2	0.24	0.008	0.000	−0.015
	4	6.98	0.249	0.239	0.254
	5	0.72	0.030	0.000	−0.022
	7	0.24	—	0.074	0.091
 [e]	1	—	—	0.226	0.228
	3	0.46	0.016	0.003	−0.012
	4	5.23	0.187	0.184	0.172
	7	0.23	—	0.088	0.112
 [e]	1	—	—	0.125	0.108
	2	4.62	0.165	0.159	0.165
	7	0.16	—	0.049	0.060

 *f*	1	—	—	0.159	0.170
	2	0.16	0.006	0.028	0.024
	3	2.38	0.074	0.081	0.078
	4	—	—	0.130	0.138
	5	—	—	0.105	0.097
	6	2.72	0.097	0.084	0.087
	7	0.48	0.017	0.016	0.004
	8	4.96	0.177	0.142	0.147
	13	0.14	—	0.044	0.060
 *f*	1	—	—	0.144	0.150
	2	0.14	0.005	0.024	0.018
	3	2.24	0.080	0.078	0.076
	4	—	—	0.114	0.113
	13	0.14	—	0.039	0.050
 *f*	1	—	—	0.180	0.192
	2	2.35	0.084	0.073	0.074
	5	3.17	0.113	0.144	0.137
	6	1.41	0.050	0.059	0.053
	9	—	—	0.001	−0.007
	11	0.06	—	0.043	0.052
 *e*	1	—	—	0.161	0.162
	2	2.12	0.076	0.071	0.073
	3	1.66	0.059	0.062	0.056
	4	4.70	0.168	0.167	0.174
	9	—	—	0.000	−0.009
	11	<0.04	—	0.038	0.044

(continued)

TABLE 3 (continued)

Compound	Position	a_{expt}[a]	ρ_{expt}[b]	ρ_{HMO}[c]	ρ_{Mac}[d]
 e	1	4.61	0.165	0.181	0.192
	2	—	—	0.082	0.087
	3	0.22	0.008	0.045	0.029
	4	4.49	0.160	0.170	0.174
	9	—	—	0.001	—0.008
	11	0.11	—	0.020	0.026
 f	1	—	—	0.270	0.266
	2	2.33	0.083	0.084	0.082
	3	1.46	0.052	0.060	0.054
	4	7.61	0.272	0.273	0.270
	7	<0.10	—	0.168	0.192
 f	1	—	—	0.240	0.235
	2	1.88	0.067	0.066	0.064
	7	—	—	0.127	0.138
 f	1	—	—	0.155	0.159
	2	0.00	0.000	0.023	0.020
	3	2.38	0.085	0.084	0.084
	4	—	—	0.123	0.124
	5	—	—	0.112	0.111
	6	2.70	0.096	0.085	0.086
	7	0.52	0.019	0.018	0.014
	8	5.08	0.181	0.147	0.150
	13	—	—	0.043	0.049
 f	1	—	—	0.145	0.148
	2	0.20	0.007	0.020	0.017
	3	2.41	0.085	0.080	0.080
	4	—	—	0.113	0.112
	13	—	—	0.040	0.044

 *f*	1	—	—	0.172	0.175
	2	2.13	0.076	0.067	0.067
	5	3.72	0.133	0.160	0.160
	6	1.54	0.055	0.062	0.061
	9	—	—	0.000	−0.003
	11	0.04	—	0.038	0.041

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[a] Hyperfine coupling constants in gauss. [b] "Experimental" spin density estimated from a_{expt} and McConnell's relation with $Q^{H}_{CH} = -28.0$ gauss. [c] Spin densities calculated using Hückel MO model. [d] Spin densities calculated using McLachlan method. [e] Hyperfine coupling constants reported in Ref. 18. [f] Hyperfine coupling constants reported in Ref's 14 and 15.

molecules of Table 3 in which such hyperfine splittings are observed; predicted and experimental hfs agree within ±0.04 gauss, compared with the error limits of ±0.02 to ±0.05 gauss that are quoted usually for coupling constants. A three-term equation including a cross-term in the overlap contribution, $S_{C'Si}$, from electron density in the bond between C′ and Si was tried also but produced no better fit to the experimental data.

The agreement produced by the two-term relation is not very general: e.g., it would predict a silyl-methyl hyperfine coupling constant of ca. 1.5 gauss for $\cdot CH_2SiMe_3$ radical in contrast with the observed value of $a_{SiCH_3} = 0.41$ gauss [37]. Even the invocation of localized charge effects should not be expected to explain this factor-of-three disagreement [38].

The mechanism of silyl-methyl proton hyperfine interaction is of current interest [37], but most investigators' attention has been given to systems in which Me_3Si is β to the radical center (e.g., $\cdot CH_2CH_2SiMe_3$) [39, 40]. A simple comparison of the methyl proton hyperfine coupling constants for the $\cdot CH_2MMe_3$ series suggests that the trend may reflect the increasing distance from the radical center to the methyl protons [37]: for M = C, Si, Ge, Sn, a_{MCH_3} (gauss) = 1.00, 0.41, <0.02, 0.17, respectively. The limited success of our empirical two-term relation in fitting a_{SiCH_3} for radical anions supports the validity of models that place unpaired spin density at silicon, i.e., homoconjugative models involving "$d_\pi \leftarrow p_\pi$" interactions that were also suggested by the investigators of $\cdot CH_2MMe_3$ systems [37].

Catenated silicon compounds. Electronic spectroscopic evidence from studies of polysilanes has been interpreted as suggesting the existence of delocalized antibonding MOs with appreciable 3*d* and perhaps 4*s* and 4*p* character [41—43], and experimental evidence reported from our laboratories supports the existence of delocalized, perhaps (*d*—*d*)-π, molecular orbitals for cyclic catenated organosilicon compounds [21, 44, 45]. Evidence for delocalized MOs extending from carbon π-electron systems to silicon atoms is contradictory: Schweig and coworkers interpret the results of photoelectron spectroscopic measurements on dimethyldivinylsilane to indicate conjugation through the silicon atom [5]. On the other hand electron delocalization in diarylsilane anion radicals is less than in diarylmethanes [47]. Also, Pitt and coworkers have reported the determination of ionization potentials and reduction potentials for a series of α-naphthyl- and phenyl-substituted polysilanes [46], with results indicating only a small increase in stabilization of the molecules as the Si—Si chain length is increased: $E_{1/2}$ for Naph-$(SiMe_2)_n$-Me (n = 1—3) was constant within experimental error.

Radical anions of pentamethyldisilanylbenzene and tris(trimethylsilyl)silylbenzene were investigated by ESR spectroscopy to see if (*d*—*d*)-π interactions among silicon atoms would influence electron distribution in these species. Significant Si—Si conjugative interactions would be expected to produce a shift of π-electron density away from the ring π-electron system into the Si—Si system. Such a shift should be especially noticeable in anion radicals because of the C—Si electronegativity difference, and should be observable as decreases in hyperfine coupling constants of the ring protons. However, the two catenated radical anions actually show only small changes in their ring proton hyperfine splittings compared to trimethylsilylbenzene.

MO calculations for the catenated molecules were made using the coulomb parameter derived from Me_3Si as a first approximation. An upper limit of 0.2 was established for the Si—Si resonance integral, β_{SiSi}: larger values predicted migration of spin density from the ring greater than that observed. Because of the large number of MO parameters and small number of ESR splittings in these systems, no systematic attempt was made to derive independent MO parameters. Small variations in the heteroatom parameters did produce improved agreement between calculated and experimental spin densities, but the obvious conclusion that there is little participation by the secondary silicon atom(s) remain unchanged. The silicon atom directly bonded to the phenyl ring participated in the ring π system to about the same extent as in trimethylsilylbenzene.

Phenyl-substituted silicon chains appear to be poor systems in which to look for $(d$—$d)$-π effects, probably because the greater electron affinity of the phenyl group effectively localizes the unpaired electron in the aromatic ring.

Conclusion

The ESR spectra of organosilyl-substituted benzenes can be understood in terms of the stabilization of one of the two nearly-degenerate antibonding MOs of benzene. When organometal-substituents are treated as pseudoheteroatoms in the molecular π-electron system, the following parameters are adequate to predict ESR results for substituted benzene, biphenyl and naphthalene anions: $h_{Si} = -2.0$, $k_{CSi} = 0.7$; $h_{Ge} = -1.45$, $k_{CGe} = 0.4$. MO calculations using these parameters predict significant unpaired electron density on the heteroatom of organometal-substituted molecules. Correlation of silyl-methyl proton hyperfine splittings with MO spin densities requires the use of a relation with at least two terms, although the sparsity of experimental data and the narrow range of variation of existing data make the exact relationship elusive.

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