Electron Spin Resonance Studies of Silicon- and Germanium-Substituted Anion Radicals

A. L. Allred and Lee W. Bush[1]

Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received September 21, 1967*

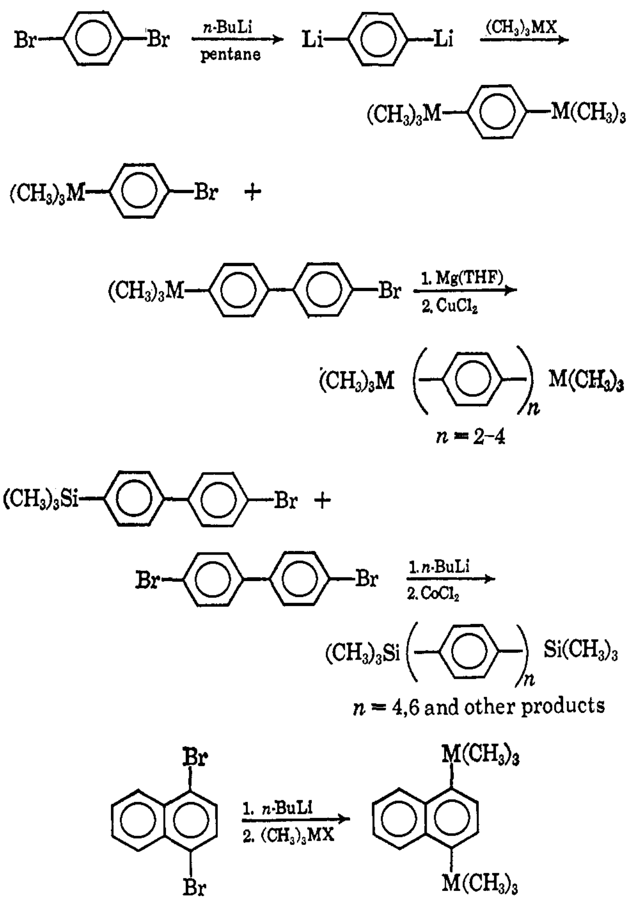
Abstract: Trimethylsilyl- and trimethylgermyl-substituted polyphenyl and naphthalene compounds and their anion radicals have been prepared. By the techniques of electron spin resonance, polarography, and ultraviolet spectroscopy, experimental data were acquired which are comparable to quantities predicted from a simple Hückel molecular orbital model. This work confirms previously published heteroatom parameters and π-bond orders for silicon–carbon and germanium–carbon bonds.

The influence of a substituent on an aromatic π-electron system is ascertained readily if the spin density of the ion radical can be measured by electron spin resonance techniques. Bedford, *et al.*,[2] interpreted the electron spin resonance spectra of the radicals of monosubstituted trimethylsilyl and trimethylgermyl derivatives of benzene in terms of a π-electron withdrawal by the substituent. Curtis and Allred[3] studied the mono- and disubstituted derivatives of biphenyl to measure π-electron withdrawal in a quantitative manner. The experimental spin densities and reduction potentials from the monosubstituted biphenyls were used to obtain a set of heteroatom parameters corresponding to the Coulomb integral, $\alpha_M = \alpha_0 + h_M\beta_0$, and the resonance integral, $\beta_{CM} = k_{CM}\beta_0$. A simple Hückel molecular orbital calculation on these compounds for various values of α_M and β_{CM} produced agreement with the experimental data when the parameters were $h = -1.20$ and $k = 0.450$ for $(CH_3)_3Si$–, and $h = -1.05$, and $k = 0.300$ for $(CH_3)_3Ge$–. These calculations predicted a π-bond order of 0.18 for the silicon–carbon bond and 0.13 for the germanium–carbon bond.

The purpose of this work is to investigate a large number of trimethylsilyl- and trimethylgermyl-substituted compounds by the same methods as those in ref 3. In this way, the generality of the heteroatom parameters and the calculated π-bond orders can be tested.

Results

The neutral organometallic compounds,[4] $(CH_3)_3M(C_6H_4)_nM(CH_3)_3$ and $1,4\text{-}((CH_3)_3M)_2(C_{10}H_6)$ (n = 1, 2–4; M = Si, Ge) were synthesized either by the reaction of lithium derivatives with $(CH_3)_3MX$[3] or by coupling reactions. The preparation of the naphthalene derivatives involved two successive treatments with n-butyllithium and $(CH_3)_3MX$. This reaction proceeded in a stepwise fashion probably because of the low solubility of the monolithium monobromonaphthalene intermediate.



M = Si, Ge

Electron Spin Resonance. Solutions, ~5 × 10^{-4} *M*, of the uninegative radicals were prepared in tetrahydrofuran (THF) by reduction of the organosilicon and organogermanium compounds with alkali metal. The corresponding esr spectra were recorded at −50° and several are presented in Figures 1–6. For each experimental spectrum the coupling constants and line width were estimated and then used to construct a simulated spectrum. The simulated spectra were obtained with the aid of a CDC 3400 computer and CALCOMP plotter and are presented below the experimental spectra in Figures 1–6. The magnitudes of the splitting constants were varied by a trial-and-error procedure until a good match of peak position and intensity was obtained between the calculated and experimental spectra. The assignment of splittings was assisted by the use of theo-

---

[1] National Institutes of Health Predoctoral Fellow.

[2] J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 59, 53 (1963).

[3] M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, 87, 2554 (1965).

[4] All the polyphenyl compounds in this paper are the *para*-substituted isomers. In naming the compounds, generally only the substituent position will be given. For example, 4,4''-bis(trimethylsilyl)-1,1':4',1''-terphenyl will be shortened to 4,4''-bis(trimethylsilyl)-terphenyl.

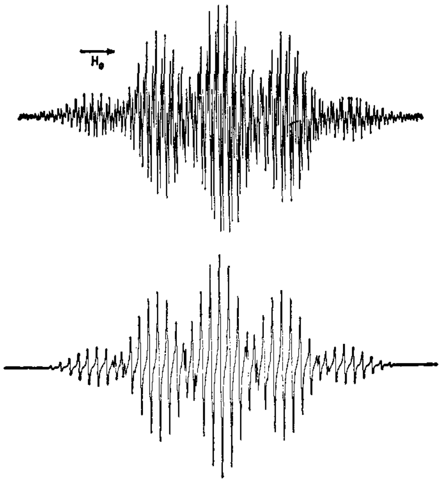


Figure 1. 1,4-Bis(trimethylsilyl)benzenide. The computed spectrum (bottom) does not reflect the observed splitting due to potassium.

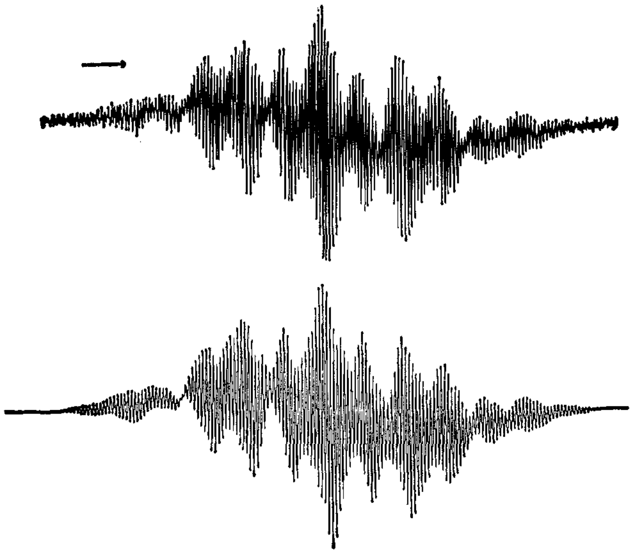


Figure 2. 4,4′′-Bis(trimethylsilyl)terphenylide. For all spectra presented here, the applied magnetic field increases from left to right, and the lengths of the arrows correspond to a field change of 1 G. For each radical, the computed spectrum based on the a_i values in Table I is shown below the experimental spectrum.

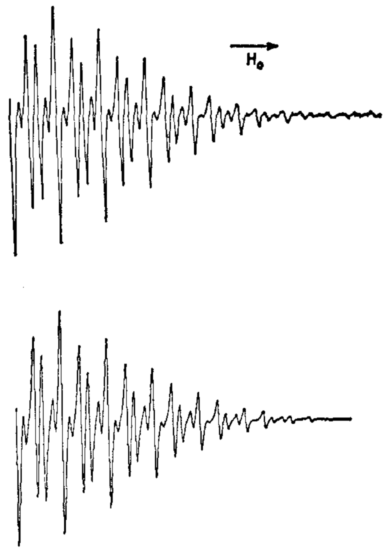


Figure 3. 4,4′′-Bis(trimethylgermyl)terphenylide.

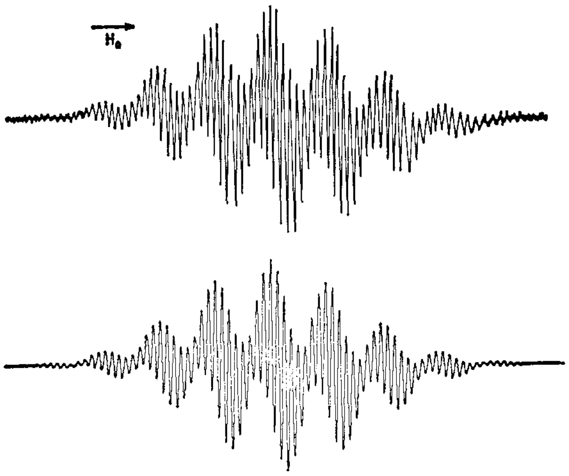


Figure 4. 4,4′′′-Bis(trimethylgermyl)quaterphenylide.

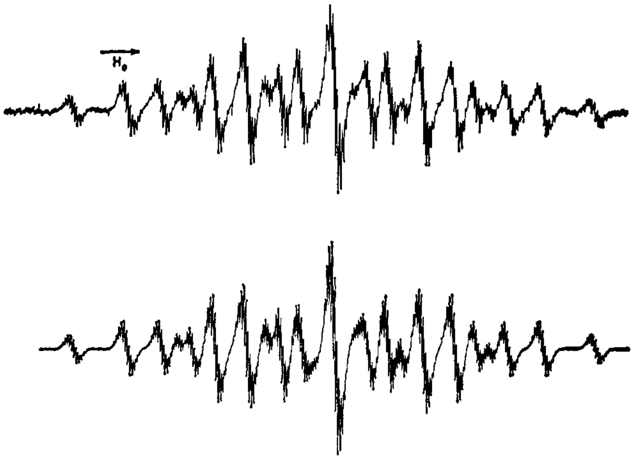


Figure 5. 1,4-Bis(trimethylsilyl)naphthalenide.

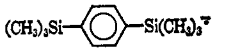
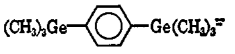
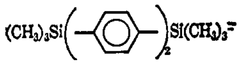
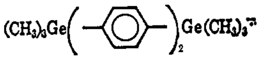
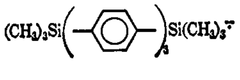
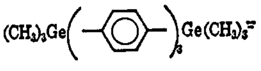
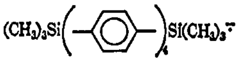
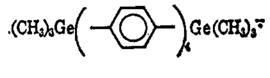
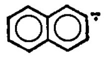
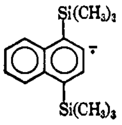
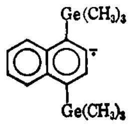
Figure 6. 1,4-Bis(trimethylgermyl)naphthalenide.

retical predictions and analogies with the parent compounds. Each spectrum will be discussed individually below. The numbering systems used and the splitting constants for all the spectra are listed in Table I. The numbering of the atoms in Table I is shown in Chart I.

Potassium 1,4-bis(trimethylsilyl)benzenide was prepared at −63° (chloroform–Dry Ice) as a yellow solution which at −50° gave the spectrum shown in Figure 1. No reaction appeared to occur when sodium was used as the reducing agent. The anion was stable for several hours at room temperature.

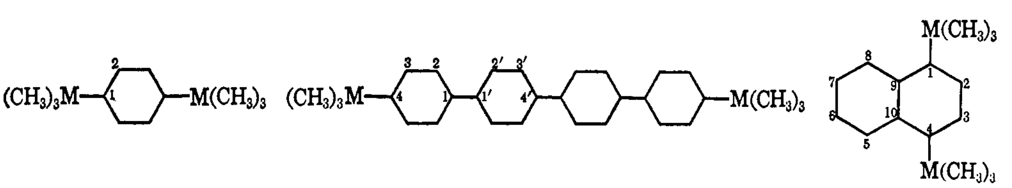
The calculated plot (bottom of Figure 1) is based on four equivalent ring protons and 18 equivalent methyl

Table I. Splitting Constants and Spin Densities of Anion Radicals

Anion	Atom[a]	a_i	Exptl ρ_i	Hückel ρ_i	McLachlan ρ_i
	1	...	...	0.182	0.224
	2	1.83	0.065	0.058	0.035
	Si	...	...	0.202	0.206
	CH_3	0.27	0.010	...	...
	K	0.09	...	...	...
	1	...	...	0.153	0.189
	2	1.88	0.067	0.046	0.026
	Ge	...	...	0.255	0.258
	4	...	...	0.130	0.170
	3	0.14[b]	0.005[b]	0.024	−0.008
	2	2.24	0.080	0.069	0.077
	1	...	...	0.103	0.110
	Si	...	...	0.081	0.082
	CH_3	0.14	0.005	...	...
	4	...	...	0.132	0.175
	3	0.20[b]	0.007[b]	0.021	−0.015
	2	2.41	0.085	0.072	0.083
	1	...	...	0.104	0.109
	Ge	...	...	0.080	0.080
	4	...	...	0.083	0.112
	3	0.32	0.011	0.012	−0.013
	2	1.83	0.065	0.052	0.065
	1	...	...	0.056	0.052
	1′	...	...	0.105	0.125
	2′	0.90	0.032	0.043	0.034
	Si	...	...	0.041	0.041
	CH_3	0.08	0.003	...	...
	4	...	...	0.084	0.114
	3	0.40	0.014	0.009	−0.018
	2	1.94	0.069	0.055	0.070
	1	...	...	0.053	0.047
	1′	...	...	0.112	0.133
	2′	0.97	0.035	0.045	0.034
	Ge	...	...	0.034	0.034
	4	...	...	0.055	0.075
	3	...	...	0.007	−0.012
	2	1.35	0.048	0.037	0.048
	1	...	...	0.033	0.027
	1′	...	...	0.086	0.105
	2′	...	...	0.028	0.013
	3′	1.35	0.048	0.043	0.043
	4′	...	...	0.074	0.083
	Si	...	...	0.024	0.024
	4	...	...	0.054	0.074
	3	0.16	0.006	0.005	−0.014
	2	1.32	0.047	0.038	0.051
	1	...	...	0.030	0.022
	1′	...	...	0.090	0.111
	2′	0.32	0.011	0.027	0.012
	3′	1.32	0.047	0.045	0.046
	4′	...	...	0.077	0.085
	Ge	...	...	0.018	0.018
	1	4.90[c]	0.175	0.181	0.229
	2	1.83[c]	0.065	0.069	0.043
	9	...	...	0.0	−0.044
	1	...	...	0.169	0.211
	2	2.35	0.084	0.071	0.051
	5	3.17	0.113	0.126	0.158
	6	1.41	0.050	0.053	0.034
	9	...	...	0.001	−0.034
	Si	...	...	0.080	0.079
	CH_3	0.06	0.002	...	...
	1	...	...	0.165	0.208
	2	2.13	0.076	0.066	0.044
	5	3.72	0.133	0.143	0.181
	6	1.54	0.055	0.057	0.036
	9	...	...	0.000	−0.037
	Ge	...	...	0.069	0.068
	CH_3	0.04	0.001	...	...

[a] The numbering of atoms is shown in Chart I. [b] Ref 3. [c] A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

Chart I



protons. The finest observed splitting (0.09 G) is caused by the associated potassium nucleus. With a nuclear spin of $^3/_2$, the potassium causes splitting of each major line into four lines of equal intensity. After considering the intensity contribution from a multiple overlap ($a_{CH_3} = 3a_{K^+}$), the observed spectrum can be duplicated by splitting each line from the lower plot in Figure 1 into four lines of equal intensity. At higher temperatures the finest splitting became less resolved.

Potassium 1,4-bis(trimethylgermyl)benzenide was observed as a yellow solution when reduction was carried out at −78° (methanol–Dry Ice). The anion is less stable than the silicon analog.

The experimental spectrum was matched by a calculated spectrum based on splitting arising from only the four equivalent ring protons and a line width of 0.17 G.

Sodium 4,4′′-bis(trimethylsilyl)terphenylide is green in solution at room temperature.[5] The resulting esr spectrum is shown in Figure 2. A low anion concentration ($\sim 10^{-4}$ *M*) is a prerequisite for a well-resolved spectrum.

The large number of lines arises from the presence of a small methyl splitting. The spectrum was analyzed to give coupling constants for the three sets of four equivalent protons in addition to the methyl splitting. The best fit in intensities was obtained by assuming that $a_2 = 4(a_{CH_3})$ and that the line width is 0.06 G. The resulting calculated plot is presented in Figure 2.

Sodium 4,4′′-bis(trimethylgermyl)terphenylide, which also gives a green solution, exhibits a spectrum with positions and intensities similar to those of a simulated spectrum based on the a_i values in Table I and a line width of 0.06 G.

Sodium 4,4′′′-bis(trimethylsilyl)quaterphenylide was present as a red-orange anion when the neutral compound was reduced at room temperature. Several different concentrations gave only a spectrum having rather broad lines ($\sim$0.9 G).

The partially resolved spectrum of nine lines was analyzed by assuming $a_3 = a_9$. The broadness of the lines probably arises from an envelope of peaks due to unresolved splitting by the hydrogens in the methyl groups and at positions 3 and 2′. With increasing chain length of the radical, spin density is lowered and coupling constants become smaller.

Sodium 4,4′′′-bis(trimethylgermyl)quaterphenylide was observed as a red-orange solution when the reduction was carried out at room temperature. The resulting esr spectrum is shown in Figure 4.

The spectrum was again analyzed by assuming that $a_3 = a_9$. A match of the computed plot with the experimental spectrum was obtained with the a_i values of 1.32, 0.16, and 0.32 G and a line width of 0.1 G. The assignment of the smaller splittings to the 3 and 2′ positions becomes rather arbitrary since both positions are predicted to have a low spin density.

Sodium 4,4′′′′′-bis(trimethylsilyl)sexiphenylide was formed by reduction of the parent compound at room temperature. The esr spectrum of the dark orange anion involved a complex splitting pattern, as expected, and was not analyzed in detail.

The radical anions of the other quinquephenyl- and sexiphenyl-substituted compounds were not prepared since they probably would not contribute any new data. The effect of the substituent is already very small in the quaterphenyl case. In addition, since a large number of lines would be expected, complete interpretation would be very difficult.

Sodium 1,4-bis(trimethylsilyl)naphthalenide gave the esr spectrum shown in Figure 5. The anion was observed as a yellow solution at room temperature. The spectrum was interpreted in terms of three sets of two equivalent protons, a small splitting from the methyl protons, and a line width of 0.045 G.

Sodium 1,4-bis(trimethylgermyl)naphthalenide was observed as a yellow solution when the reduction was carried out at −63°. The esr spectrum is presented in Figure 6. The anion appears to be stable at room temperature for at least several weeks as shown by esr. For low anion concentrations, $\sim 10^{-4}$ *M*, splitting from the trimethylgermyl groups was observed. This small splitting disappeared with an increase in anion concentration. The computed spectrum is based on three triplets (which could be measured directly), the small methyl splitting, and a line width of 0.04 G.

The assignment of the splitting constants for these naphthalene anions can become somewhat arbitrary for the ring protons since all the major splittings are triplets. The assignments result from a consideration of a theoretical prediction of spin density distribution and of the logical perturbation by an electron-withdrawing substituent of the distribution in the parent compound, naphthalene. The observed splitting constants for naphthalenide are $\alpha_1 = 4.95$ G and $\alpha_2 = 1.87$ G. An electron-withdrawing substituent should increase the electron density on the ring to which it is attached. This would require a corresponding decrease in electron density on the adjacent ring. On this basis the splitting constants should be greater than 1.87 for position 2, less than 4.95 for position 5, and less than 1.87 for position 6.

Polarography. All of the silyl and germyl derivatives, except 1,4-bis(trimethylgermyl)benzene, showed a one-electron reversible wave in dimethylformamide solutions. In the polyphenyls a second wave was observed with a total diffusion current twice that of the first wave, indicating a two-electron reduction.

Reversibility was investigated by observing the line width at half-height in ac polarographs and the relationship between the dc half-wave potential and the ac peak potential. The initial waves satisfied the re-

---

(5) The substituted terphenyl and quaterphenyl solutions all showed a second color change (to blue) on prolonged exposure to sodium. The blue solutions do not exhibit esr spectra and probably contain the dianions.

Table II. Polarographic Data and Energies from Reduction Potentials and from HMO Calculations

	1st wave				2nd wave		
	$-E_{\mathrm{peak(ac)}}$, V[a]		$-\epsilon_{m+1}$ (units of β)		Potentials, V (Ag|AgNO$_3$ ref)		
	Ag|AgNO$_3$	Hg pool	Exptl	HMO	$-E_{1/2\mathrm{(dc)}}$	$-E_{\mathrm{peak(ac)}}$	Half-width[b]
$(CH_3)_3Si(C_6H_4)Si(CH_3)_3$	3.45	2.35	0.812	0.773	...[c]	...[c]	...
$(CH_3)_3Ge(C_6H_4)Ge(CH_3)_3$	<3.50	...	...	0.818	...[c]	...[c]	...
$(CH_3)_3Si(C_6H_4)_2Si(CH_3)_3$	2.97	1.87	0.612	0.631	~3.3	~3.35	>120
$(CH_3)_3Ge(C_6H_4)_2Ge(CH_3)_3$	3.04	1.94	0.641	0.664	~3.3	~3.4	...
$(CH_3)_3Si(C_6H_4)_3Si(CH_3)_3$	2.79	1.69	0.538	0.557	3.07	3.08	105
$(CH_3)_3Ge(C_6H_4)_3Ge(CH_3)_3$	2.83	1.73	0.554	0.577	3.14	3.15	>120
$(CH_3)_3Si(C_6H_4)_4Si(CH_3)_3$	2.71	1.61	0.504	0.516	2.90	2.90	105
$(CH_3)_3Ge(C_6H_4)_4Ge(CH_3)_3$	2.71	1.61	0.504	0.529	2.92	2.93	110
$((CH_3)_3Si)_2C_{10}H_6$	2.90	1.80	0.583	0.545	...[c]	...[c]	...
$((CH_3)_3Ge)_2C_{10}H_6$	2.96	1.86	0.608	0.585	...[c]	...[c]	...

[a] The potentials were observed with respect to a Ag|AgNO$_3$ electrode at a precision of ±0.01 V. [b] Width in millivolts at half-height. [c] Not observed.

quirements for reversibility, a 90-mV line width, and $E_{1/2\mathrm{(dc)}} = E_{\mathrm{peak(ac)}}$,[6] within experimental error.

1,4-Bis(trimethylsilyl)benzene showed one reversible wave just before the solvent reduction wave which occurs at about −3.5 V. The former wave was observable in ac but not dc polarography. Since the solvent reduction is irreversible, ac polarography permits observation of an additional 100 mV which includes the reversible wave at −3.45 V.

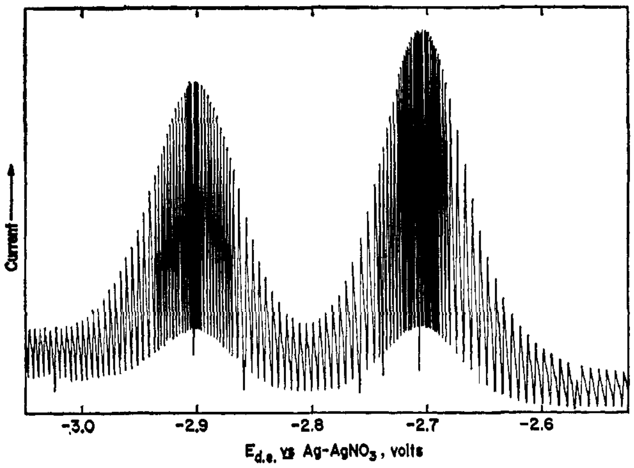


Figure 7. Ac polarogram of 4,4‴-bis(trimethylsilyl)quaterphenyl.

The corresponding germanium compound failed to show any reversible wave before solvent reduction.

The substituted polyphenyls exhibited two waves. The first wave was always reversible and occurred at increasingly less negative potentials with increasing length of the polyphenyl chain. The second wave became more nearly reversible as the length of the polyphenyl chain increased. The potentials and line-width data establishing the trend in reversibility for the second wave are given in Table II.

The ac polarogram (Figure 7) of 4,4‴-bis(trimethylsilyl)quaterphenyl contains the most nearly reversible second wave observed. This second wave decreases in amplitude and symmetry as the polyphenyl chain is shortened until it almost disappears (indicating complete irreversibility) in 4,4′-bis(trimethylgermyl)biphenyl.

The second wave probably corresponds to the formation of the dianion species which was observed in the preparation of radical anions for esr. The observed partial reversibility could be due to a rapid chemical reaction of the dianion species. Probably this reaction involves the cleavage of trimethylsilyl or trimethylgermyl groups.

Each of the substituted naphthalene compounds shows only one wave which is completely reversible.

To permit a correlation of the polarographic results with the calculated energies of the lowest unoccupied π orbitals, the potential data for the first wave will be treated in a manner that produces "experimental" values of the energy of the lowest unoccupied π molecular orbital. A common and useful procedure is to assume that the energies of the lowest unoccupied orbital and the half-wave potential are directly related.[7] By plotting half-wave potentials (determined in dimethylformamide) *vs.* the calculated energies of the lowest unoccupied orbitals for several polycyclic aromatic hydrocarbons, Streitwieser and Schwager[8] obtained a straight line described by the equation

$$E_{1/2}(\mathrm{DMF}) = (2.407 \pm 0.182)\epsilon_{m+1} - (0.396 \pm 0.093) \quad (1)$$

The experimental reduction potentials in this work were taken with a different reference electrode from that used by Streitwieser and Schwager. The potentials, $E_{\mathrm{peak(ac)}}$, of biphenyl and naphthalene were used as standards to find the average correction of +1.10 V for a change from a silver nitrate (in DMF)–silver reference electrode to a mercury pool. The corrected potentials, $E_{\mathrm{peak(ac)}}$, are listed in Table II. The energies of the lowest unoccupied orbital, ϵ_{m+1}(exptl) were calculated from the corrected values and eq 1 and are also presented in Table II.

Ultraviolet Spectra. The neutral trimethylsilyl and trimethylgermyl derivatives all exhibit spectra with features similar to those of the parent hydrocarbons. The frequencies of the broad p bands, corresponding to the $\pi_m{}^2 \rightarrow \pi_m\pi_{m+1}$ transitions, are presented in Table III.

The observed transitions can also be expressed in terms of the energy difference, $\epsilon_{m+1} - \epsilon_m$, in units of β

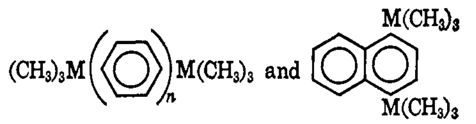
---

(6) D. E. Smith, "Electroanalytical Chemistry," Vol. I, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, Chapter 1.

(7) A. Maccoll, *Nature*, **163**, 178 (1949).

(8) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

Table III. Ultraviolet Spectra (p Band) of



	ν_{obsd} (cm^{-1}) × 10^{-4}	Molar absorptivity × 10^{-3}	$-(\epsilon_{m+1} - \epsilon_m)^a$	
			Exptl Eq 2	Calcd HMO
$(CH_3)_3Si(C_6H_4)Si(CH_3)_3$	4.43	17	1.77	1.75
$(CH_3)_3Ge(C_6H_4)Ge(CH_3)_3$	4.48	15	1.80	1.78
$(CH_3)_3Si(C_6H_4)_2Si(CH_3)_3$	3.81	30	1.45	1.33
$(CH_3)_3Ge(C_6H_4)_2$-$Ge(CH_3)_3$	3.85	29	1.47	1.35
$(CH_3)_3Si(C_6H_4)_3Si(CH_3)_3$	3.48	39	1.28	1.15
$(CH_3)_3Ge(C_6H_4)_3$-$Ge(CH_3)_3$	3.50	44	1.29	1.16
$(CH_3)_3Si(C_6H_4)_4Si(CH_3)_3$	3.32	55	1.19	1.05
$(CH_3)_3Ge(C_6H_4)_4$-$Ge(CH_3)_3$	3.32	57	1.19	1.06
$[(CH_3)_3Si]_2C_{10}H_6$	3.33^b	8	1.20	1.16
$[(CH_3)_3Ge]_2C_{10}H_6$	3.35^b	8	1.21	1.18

[a] In units of β. [b] Vibrational fine structure observed.

by application of the equation

$$\nu(\text{cm}^{-1}) = (19{,}020 \pm 330)(\epsilon_{m+1} - \epsilon_m) + (10{,}520 \pm 340) \quad (2)$$

which was obtained by Streitwieser[9] from a plot of the frequency of the p band of a number of polycyclic hydrocarbons as a function of the calculated (HMO) transition energies. The $(\epsilon_{m+1} - \epsilon_m)$ values from this equation are presented in Table III under "Exptl."

Calculations. Energies and spin densities were calculated by the Hückel molecular orbital method. The trimethylsilyl and trimethylgermyl groups were treated as heteroatoms having the Coulomb and resonance integrals stated in the introductory section, and the auxiliary inductive parameter for the contiguous ring carbon was 0.1.[10] The Hückel spin densities were corrected for configuration interaction by McLachlan's method[11] with λ equal to 1.2.[3] All molecular orbital calculations were carried out on a CDC 3400 computer for which the input data were the H matrix components and the output data included charge densities, π bond orders, Hückel energy levels in units of β, and the Hückel and McLachlan spin densities.

The calculated spin densities are presented in Table I. The calculated energies, ϵ_{m+1}, for the level which becomes occupied upon reduction are listed in Table II with the polarographic data. The calculated energies in Table III for the p-band of the uv spectra are differences between the highest occupied and lowest normally unoccupied molecular orbitals.

The observed splitting constants were related to experimental spin densities on the adjacent carbon atoms through the relationship, $a_i = Q\rho_i$.[12] The value of Q varies from 22 to 30 G in the literature and appears to be somewhat dependent on the aromatic compound being considered. A value of 28 G was chosen here to remain consistent with earlier work.[3]

Discussion

The compounds can be divided into three groups, substituted polyphenyls, substituted benzenes, and substituted naphthalenes, and each will be discussed separately below.

Substituted Polyphenyls. The heteroatom parameters were based[3] on the splitting constants and reduction potentials of the monosubstituted biphenyls, trimethylsilylbiphenyl and trimethylgermylbiphenyl, and, as demonstrated in Table I, give theoretical McLachlan spin densities which are in excellent agreement with the experimental spin densities of the compounds, $(CH_3)_3M(C_6H_4)_nM(CH_3)_3$ (M = Si, Ge; n = 2–4). Although the signs of the coupling constants are not obtainable by the techniques employed, the agreement between predicted and observed spin densities indicates that the sign of the spin density at position 3 is negative.

The relative π-electron withdrawing ability of the trimethylsilyl and trimethylgermyl groups is demonstrated in two ways in the esr data. The positions of relatively large spin density have slightly less spin density when the trimethylsilyl group is substituted, compared to the trimethylgermyl-containing compounds. In addition, methyl spin density is observed in the esr spectra of the trimethylsilyl-substituted compounds. These observations indicate a larger amount of spin density on the trimethylsilyl group and thus imply a stronger π-electron withdrawal by silicon relative to germanium.

The expected increased stability of the radical anions with increasing length of the polyphenyl chain and the decreased substituent effect in the larger polyphenyls can be noted in both the esr and polarographic data. The decreasing energy of the lowest unoccupied molecular orbital, the increasing ease of dianion formation, and the decrease in the magnitude of the methyl splitting in the trimethylsilyl group all indicate the increasing ability of the polyphenyl chain to accommodate electron density as the chain length increases. A corollary to this observation is the decreased perturbation caused by the substituent attached to the aromatic system. This can be noted directly by observing the increasing similarity between the coupling constants of the substituted and unsubstituted compounds[13] as the polyphenyl chain is lengthened. This effect is found also in the very small differences in the values of the reduction potentials and the ultraviolet transitions that are observed for the trimethylsilyl- and trimethylgermyl-substituted quaterphenyls.

Since the $\pi_m^2 \rightarrow \pi_m\pi_{m+1}$ transition, corresponding to the p band of the ultraviolet spectrum, is nondegenerate and of unique symmetry, the frequency of the p band can be used as an independent check on the validity of the Hückel calculations.[14] In all cases the spectra greatly resemble the spectra of the parent hydrocarbons. The trimethylsilyl and trimethylgermyl substituents can be considered to contribute a high-energy empty orbital to the π-electron system. The effect is to lower the energy of both the highest occupied and

---

(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 217.

(10) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

(11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(12) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); T. R. Tuttle, R. L. Ward, and S. I. Weissman, *ibid.*, **25**, 189 (1956).

(13) L. W. Bush, Thesis, Northwestern University, 1967.

(14) M. D. Curtis, R. K. Lee, and A. L. Allred, *J. Am. Chem. Soc.*, **89**, 5150 (1967).

lowest unoccupied orbitals, but the latter to a larger degree. The ultraviolet spectra thus give an experimental measure of the substituent effect by observation of the energy of the $\pi \rightarrow \pi^*$ transition.

The polyphenyl derivatives all exhibited the expected broad p band which shifts to longer wavelengths with an increase in the length of the polyphenyl chain.

The correlations of half-wave potentials and of the band in the ultraviolet with Hückel energies provides an independent check on the validity of the heteroatom parameters. The agreement appears to be reasonable in both cases. The differences in agreement are of the same magnitude and direction in the substituted and parent compounds. Thus, it appears that any change in the calculated energies would have to be made by an improvement in the molecular orbital calculations.

Since the heteroatom parameters predict experimentally observable properties in a satisfactory manner, the corresponding Hückel coefficients can be used to estimate the π bond order between the heteroatom and the aromatic ring. For each neutral compound the calculated bond orders, $p^{\pi}_{C-Si} = 0.18$ or $p^{\pi}_{C-Ge} = 0.13$, agreed with those of Curtis and Allred.[3] Since the same heteroatom parameters were used, this agreement is expected.

Substituted Benzenes. The esr spectrum for 1,4-bis(trimethylsilyl)benzenide has been reported in the literature.[15] The esr spectrum as recorded at room temperature was relatively unresolved, but the coupling constants for the ring and methyl protons agree with the values found in this work. The even line spectrum, however, was analyzed[15] in terms of splitting from the protons in only one trimethylsilyl group. The resolved spectrum given in this work seems to indicate that a more likely explanation involves the association of a potassium ion with the radical anion.

The data in Tables II and III show that the agreement between the calculated and observed energy transitions in the ultraviolet is satisfactory as is the agreement between experimental and calculated energies of the lowest unoccupied orbital in 1,4-bis(trimethylsilyl)benzene. The corresponding germanium compound is expected to have a higher energy unoccupied orbital and, as observed, not have a polarographic wave before solvent reduction. Thus, a reasonable prediction of the energy separation can be accomplished with the same heteroatom parameters used for the substituted polyphenyl compounds.

The same parameters predict McLachlan spin densities that are less than one-half the values observed experimentally for the substituted benzenes. The Hückel spin densities are somewhat better but are still much lower than the observed values in addition to appearing in the opposite order.

The explanation of this poor agreement involves two phenomena, vibronic coupling and thermal equilibrium between vibronic states.[16] A small separation of states is the expected result in substituted benzenes where the degeneracy of the orbitals is lifted, and the magnitude of the orbital separation is dependent on the perturbation of the π-electron system by the substituent. Temperature-dependent coupling constants have been observed for the toluene and *t*-butylbenzene radical anions studied in the temperature range -120 to $-70°$.[16,17]

Hobey carried out calculations to determine the extent of vibronic coupling and was able to predict reasonable spin densities in some alkylbenzenes.[18,19] As emphasized by Hobey, the magnitude of the effect of vibronic coupling is strongly dependent on the separation of the energy levels. This dependence is demonstrated by the esr and polarographic data for the substituted benzenes in this work. The trimethylsilyl-substituted radical has the lower energy singularly occupied orbital and thus the largest separation in energy between the lowest two states. The trimethylgermyl compound is affected to a greater degree by vibronic interaction. Therefore, poorer agreement between observed and Hückel spin densities is predicted, and observed, for the trimethylgermyl compound relative to the trimethylsilyl analog.

Actually, the unpaired electron is spending a finite amount of time in at least two different orbitals, and experimentally a weighted average is observed. The calculated values in Table I are based on occupation of one orbital only and thus a discrepancy must result.

Methyl proton splitting from a trimethylgermyl group was not observed in 1,4-bis(trimethylgermyl)benzenide. The trimethylgermyl group is shown to be electron-withdrawing with a π bond order of 0.13 for the germanium-carbon bond, but the spin density appears to remain largely on the ring and the germanium atom. The greater delocalization of the odd electron in 1,4-bis(trimethylsilyl)benzenide may account for it being so much more stable than the corresponding germanium compound.

Substituted Naphthalenes. Substituted naphthalene compounds were investigated to ascertain the possibility of extending to condensed ring systems the approach followed and the conclusions found for the polyphenyl series. Therefore, the same heteroatom parameters were used to obtain the calculated quantities in Tables I–III.

The observed ultraviolet transitions are in excellent agreement with the calculated energy difference between the lowest unoccupied and the highest occupied orbitals. The error was found to be in the same direction and of about the same magnitude as that observed in naphthalene.

The energies, obtained from polarographic reduction data, of the lowest unoccupied orbitals are also in reasonable agreement with the predicted values. Although the direction of the error is opposite to that found in the polyphenyls, the magnitude and direction of the error is the same for the substituted and unsubstituted naphthalenes, and thus the differences appear to be an inherent result of the molecular orbital calculations.

The esr spectrum of 1,4-bis(trimethylgermyl)naphthalenide contains the only observed example of hyperfine splitting from the methyl protons of a trimethylgermyl group. The magnitude of the methyl proton splitting should be a measure of the amount of spin density on the trimethylsilyl or trimethylgermyl group,

---

(15) S. P. Solodovnikov and E. A. Chernyshev, *Zh. Strukt. Khim.*, **3**, 665 (1962).

(16) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

(17) T. R. Tuttle, *J. Am. Chem. Soc.*, **84**, 1492, 2839 (1962).

(18) W. D. Hobey, *J. Chem. Phys.*, **43**, 2187 (1965).

(19) W. D. Hobey, *ibid.*, **45**, 2718 (1966).

and, therefore, the order of π-bonding ability is silicon > germanium.

The calculated McLachlan spin densities are in poor agreement with the experimental values. The Hückel values are in much better agreement, although the Hückel spin densities at atoms 2 and 3 are slightly low and are slightly high at atoms 5 and 6. The spin densities in the parent compound (naphthalene, Table I) are also in better agreement with the values predicted from Hückel theory. The spin densities calculated from the McLachlan method are in poor agreement with the observed spin densities in the majority of condensed aromatic hydrocarbons.[13]

In an effort either to produce agreement of the experimental spin densities with the McLachlan spin densities or to improve agreement with the Hückel values, the heteroatom parameters were varied over a considerable range. The plots of the calculated energy of the lowest unoccupied orbital, the spin density at atom 2, the spin density at atom 5, and the spin density at atom 6 against k_{CM} for various values of h_M were constructed as described in ref 3 and are presented in ref 13. No choice of heteroatom parameters was found that significantly improves the values used by Curtis and Allred.[3] The McLachlan spin densities failed to approach the experimental values for any choice of parameters. The plot of the Hückel spin density at atom 2 indicates that the only heteroatom parameters that improve the spin densities at this position require large values of k_{CM}. This set of parameters, however, lowers the energy of the lowest unoccupied orbital far below the experimental value.

The esr data probably provide evidence for *peri* interaction of the $(CH_3)_3M$– groups and the hydrogens at the 5 and 8 positions which are in closer proximity than each $(CH_3)_3M$ group and its *ortho* hydrogen.

peri interaction in naphthalenes, thoroughly reviewed recently,[20] causes significant changes in structure (the bromo atoms of 1,4-dibromonaphthalene are approximately 0.4 Å out of the plane of the rings[21]), ultraviolet spectra, reduction potentials (the magnitudes of $E_{1/2}$ differ appreciably for 1-methylnaphthalene and 2-methylnaphthalene),[22] and esr spectra.[23,24]

Conclusions

The heteroatom parameters, $h = -1.20$ and $k = 0.450$ for silicon and $h = -1.05$ and $k = 0.300$ for germanium, can be used to calculate spin densities, reduction potentials, and the energies of p bands generally in close agreement with experimental values.

Within the limits of the above theoretical treatment, the π-bond orders are 0.18 and 0.13 for the trimethylsilyl–ring and trimethylgermyl–ring bonds, respectively, for all of the aromatic compounds investigated.

Experimental Section

Electron spin resonance spectra were scanned with a Varian Associates V-4500 instrument equipped with a 100-kc/sec field modulation unit, a Fieldial, and a 12-in. electromagnet. The Fieldial was calibrated with the esr spectrum of potassium nitrosodisulfonate.[25]

Tetrahydrofuran (THF), purchased from Eastman Chemical Co., was purified by distillation from lithium aluminum hydride under nitrogen and transferred in a vacuum system to an apparatus containing either sodium or potassium. Solutions of the radicals were decanted into a 4-mm o.d. Pyrex tube which was then sealed. Low-temperature spectra were obtained by placing the sample in a special Varian Associates, Inc., dewar contained in the microwave cavity and then allowing evaporating liquid nitrogen to pass around the sample at a controlled rate.

The dc and ac polarograms were obtained on an instrument built by E. R. Brown and D. E. Smith of this department. The instrument employed solid-state operational amplifiers to provide stability and increase the signal-to-noise ratio. The polarograms were obtained from a three-electrode arrangement in which the working electrode was a dropping mercury electrode, the auxiliary electrode was a platinum wire, and the reference electrode was saturated silver nitrate (in DMF)–silver. The ohmic potential drop between the reference electrode and the working electrode was compensated for instrumentally.[26] The ac polarograms were obtained by superimposing a small ac potential (10-mV peak-to-peak at 40 cps) on the dc potential and then measuring the resulting ac current. All polarograms were recorded on an X-YY′ recorder, Model 480, Electro Instruments, Inc. The concentration of each compound was $\sim 10^{-3}$ *M*. Tetra-*n*-butylammonium perchlorate (0.1 *M*) was used as the supporting electrolyte and dimethylformamide (DMF) was the solvent. The DMF was Eastman Spectrograde that had been dried over calcium hydride and distilled in an all "O-ring" apparatus at 15 mm. The solutions were purged with nitrogen immediately before reduction and a nitrogen atmosphere was maintained over each solution throughout the experiment.

The ultraviolet spectra were obtained on a Cary 14 spectrometer using 1-cm quartz cells. The compounds were all approximately 2×10^{-5} *M* solutions in Spectrograde heptane (Matheson Coleman and Bell).

n-Butyllithium (15% in hexane) and trimethylchlorosilane were purchased from Foote Mineral Co. and Alfa Inorganics, respectively. The trimethylbromogermane was prepared from tetramethylgermane, bromine, and a catalytic amount of aluminum tribromide.[27] The anhydrous cupric chloride and cobalt chloride were obtained from Baker and Adamson and Alfa Inorganics, respectively. The remaining bromo-substituted aromatic compounds were purchased from Eastman Organic Chemicals and when necessary recrystallized before use. All melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

1,4-Bis(trimethylsilyl)benzene. In an atmosphere of nitrogen, 12.5 ml (0.02 mole) of *n*-butyllithium solution was added dropwise with stirring to 2.35 g (0.01 mole) of 1,4-dibromobenzene in 75 ml of pentane (dried over sodium). Stirring was continued for 24 hr at room temperature and the dilithiated derivative, a light yellow solid, was observed. Trimethylchlorosilane (2.2 g, 0.02 mole) was added dropwise at a sufficient rate to maintain refluxing, and the resulting solution was stirred for an additional 2 hr. Dilute sulfuric acid (~ 1 *M*) was added and the resulting layers were separated and washed. The pentane solution was reduced in volume to ~ 15 ml and chromatographed on a silica column using pentane as the eluent. The first eluted product, a white solid, was recrystallized from methanol: mp 88–89°, roughly 50% yield.

Anal. Calcd for $C_{12}H_{22}Si_2$: C, 64.78; H, 9.96. Found: C, 64.44; H, 9.85.

1,4-Bis(trimethylgermyl)benzene was prepared by the same procedure using 4 g of trimethylbromogermane. After recrystallization from methanol, the white solid melts at 91–92°, 50% yield.

Anal. Calcd for $C_{12}H_{22}Ge_2$: C, 46.27; H, 7.12. Found: C, 46.07; H, 7.28.

4-Bromo-4′-trimethylsilylbiphenyl. The reaction of 4,4′-dibromobiphenyl and *n*-butyllithium in a 1:1 mole ratio gives the monosubstituted lithium derivative which was allowed to react with trimethylchlorosilane: mp 91–93°, 80% yield.

---

(20) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(21) J. Trotter, *Can. J. Chem.*, **39**, 1574 (1961).

(22) L. H. Klemm and A. J. Kohlik, *J. Org. Chem.*, 28, 2044 (1963).

(23) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, 87, 129 (1965).

(24) P. H. H. Fischer and C. A. McDowell, *Can. J. Chem.*, **43**, 3400 (1965).

(25) A splitting of 13.05 G was assumed: J. J. Windle and A. K. Wiersema, *J. Chem. Phys.*, **39**, 1139 (1963).

(26) E. R. Brown, T. McCord, D. E. Smith, and D. D. DeFord, *Anal. Chem.*, 38, 1119 (1966).

(27) M. Lesbre and P. Mazerolles, *Compt. Rend.*, **246**, 1708 (1958).

An analogous reaction gave crude 4-bromo-4'-trimethylgermylbiphenyl, mp 94–98°.

4-Trimethylsilylbromobenzene was obtained by a reported[28] procedure, bp 53–56° (0.2 mm).

4-Trimethylgermylbromobenzene was prepared from 4-lithiobromobenzene and trimethylbromogermane in ether, bp 85–95° (~10 mm).

4,4''-Bis(trimethylsilyl)-1,1':4',1''-terphenyl. Magnesium turnings (1.7 g, 0.07 g-atom), 4-bromo-4'-trimethylsilylbiphenyl (8.0 g, 0.026 mole), and 4-trimethylsilylbromobenzene (5.9 g, 0.026 mole) were added to a nitrogen-flushed reaction flask containing 200 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride). The Grignard solution was refluxed for 4 hr and then cooled to room temperature. Anhydrous cupric chloride (7.4 g, 0.055 mole) was added *slowly, with caution* and vigorous stirring. This mixture was then refluxed for an additional 3 hr. At room temperature 100 ml of 6 *M* HCl was added slowly. Ethyl ether was added and the resulting layers separated. The organic layer was washed with more dilute HCl (~1 *M*) until the aqueous layer was colorless, indicating that all the copper salts have been removed. The ether layer was stripped to dryness under reduced pressure. This solid was treated twice with ~150 ml of hot ethanol and filtered. These solutions should contain 4,4'-bis(trimethylsilyl)biphenyl formed as a by-product. The solid from the filtration was treated with 400 ml of ether at reflux temperature and then filtered off. This ether solution was stripped to dryness under reduced pressure and treated with benzene. The benzene solution was chromatographed on silica using a 10% benzene–90% pentane solution as eluent. The first fraction of solid collected was recrystallized from ethanol to give white flakes: mp 198–200°, 10% yield.

Anal. Calcd for $C_{24}H_{30}Si_2$: C, 76.94; H, 8.07. Found: C, 77.63; H, 8.17.

4,4'''-Bis(trimethylsilyl)-1,1':4',1'':4'',1'''-quaterphenyl. The ether-insoluble solid from the previous reaction was recrystallized from chloroform: mp 278–280°, 5% yield. This product was obtained in a somewhat higher yield by coupling 4-bromo-4'-trimethylsilylbiphenyl with itself.

Anal. Calcd for $C_{30}H_{34}Si_2$: C, 79.93; H, 7.60. Found: C, 80.34; H, 7.44.

4,4''-Bis(trimethylgermyl)-1,1':4',1''-terphenyl was prepared by the procedure given above for the analogous silicon compound. When recrystallized from ethanol, the white flakes melted at 202–205°.

Anal. Calcd for $C_{24}H_{30}Ge_2$: C, 62.17; H, 6.52. Found: C, 61.79; H, 6.33.

4,4'''-Bis(trimethylgermyl)-1,1':4',1'':4'',1'''-quaterphenyl. The ether-insoluble solid from the 4,4''-bis(trimethylgermyl)terphenyl preparation gave the desired product when recrystallized from chloroform: mp 278–280°.

Anal. Calcd for $C_{30}H_{34}Ge_2$: C, 66.75; H, 6.34. Found: C, 66.73; H, 6.49.

4,4'''''-Bis(trimethylsilyl)-1,1':4',1'':4'',1''':4''',1'''':4'''',1'''''-sexiphenyl. 4,4'-Dibromobiphenyl (1.9 g, 0.0061 mole) and 4-bromo-4'-trimethylsilylbiphenyl (7.5 g, 0.0246 mole) were added to a nitrogen-flushed reaction flask containing 200 ml of ethyl ether (freshly distilled from lithium aluminum hydride). *n*-Butyllithium (23 ml, 0.0368 mole) was added dropwise at room temperature and the resulting solution was stirred for 1 hr. Cobalt chloride (4.7 g, 0.0368 mole) and 150 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) were added, and the resulting mixture was refluxed for 12 hr. Then at room temperature, 6 *M* HCl and additional ethyl ether were added and the layers separated. The organic layer was extracted several times with dilute aqueous HCl. The ether was removed under reduced pressure and the resulting solid extracted with two successive 150-ml portions of warm tetrahydrofuran. The remaining solid was sublimed twice (~340° at 5 mm) to obtain the desired product (roughly 5% yield).

Anal. Calcd for $C_{42}H_{42}Si_2$: C, 83.66; H, 7.02. Found: C, 84.06; H, 7.27.

1,4-Bis(trimethylsilyl)naphthalene. 1,4-Dibromonaphthalene (3 g, 0.0105 mole) was added to a nitrogen-flushed reaction flask containing 100 ml of ethyl ether (freshly distilled from lithium aluminum hydride). *n*-Butyllithium (13 ml, 0.021 mole) was added dropwise and the resulting solution stirred for 2 hr at room temperature. Trimethylchlorosilane (2.3 g, 0.021 mole) was added dropwise and stirring continued for 2 hr. Dilute sulfuric acid (~1 *M*) was added and the resulting layers were separated and washed. The ether was stripped off under reduced pressure. The resulting oil was dissolved in pentane and chromatographed on silica using pentane as the eluent. A clear oil was eluted first but failed to crystallize from methanol. The oil was dissolved in freshly distilled ethyl ether under nitrogen and 0.01 mole of *n*-butyllithium added. The solution turned yellow indicating that an exchange reaction had occurred. Trimethylchlorosilane (0.01 mole) was added to the solution and the color disappeared. Dilute sulfuric acid was added and the resulting layers were separated and washed. The ether was stripped off under reduced pressure and the resulting oil chromatographed on silica using pentane as the eluent. A white solid crystallized from the eluent and was recrystallized from methanol: mp 92–93° (lit.[29] 90–92°), ~10% yield.

Anal. Calcd for $C_{16}H_{24}Si_2$: C, 70.51; H, 8.88. Found: C, 69.88; H, 8.45.

1,4-Bis(trimethylgermyl)napthalene was prepared by the same procedure: mp 104–105°.

Anal. Calcd for $C_{16}H_{24}Ge_2$: C, 53.15; H, 6.69. Found: C, 53.10; H, 6.69.

Acknowledgments. This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center. L. W. B. expresses appreciation for a predoctoral fellowship from the Division of General Medical Sciences, United States Public Health Service. We thank Drs. E. R. Brown, D. E. Smith, and D. F. Shriver for valuable assistance.

---

(28) H. Gilman, H. W. Melvin, and J. J. Goodman, *J. Am. Chem. Soc.*, 76, 3219 (1954).

(29) D. R. Weyenberg and L. H. Toporcer, *J. Org. Chem.*, 30, 943 (1965).