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DIMETHYLSILYL- AND METHYLENE-BRIDGED AROMATIC GROUPS

I. POLAROGRAPHY AND ULTRAVIOLET SPECTROSCOPY

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SUMMARY

For the compounds $C_6H_5C_6H_4YC_6H_4C_6H_5$ and $C_6H_5C_6H_4YC_6H_4C_6H_4Y$-$C_6H_4C_6H_5$ where Y is either $-Si(CH_3)_2-$ or $-CH_2-$, reduction potentials and *p*-band positions are reported. These data as well as the UV data for several phenyl derivatives are consistent with silicon blocking, to a large extent, conjugation (little or no through conjugation) of biphenyl moieties separated by $-Si(CH_3)_2-$groups.

INTRODUCTION

Numerous investigations of the participation of 3*d* orbitals of silicon in the formation of π-bonds have been made[1-4], and the π-bond order for the silicon–aromatic ring bond has been reported[5] to be 0.18. However, diverse investigations[6-12] lead to apparently inconsistent conclusions about whether or not two aromatic groups separated by a silicon atom are conjugated with each other. The electrochemical and spectral investigations reported herein were designed to explore the possibility of this "through conjugation."

EXPERIMENTAL

Polarography

D.c. polarography and phase-selective fundamental and second harmonic a.c. polarography at 200 Hz employing positive feed-back were performed with an instrument designed and built in this laboratory[13]. Freshly distilled dimethylformamide (DMF) was used as the solvent. The supporting electrolyte was tetrabutylammonium perchlorate, TBAP, (Southwestern Analytical Laboratories, polarographic grade) which had been recrystallized from anhydrous methanol and dried in vacuum at 100° for three days before use. The solutions were 0.1 *M* in supporting electrolyte and 1.00 ($\pm$0.04) $\times 10^{-3}$ *M* in electroactive species. All solutions were thermostatted at 25° and purged with N_2 before carrying out the experiments.

The working electrode was a dropping mercury electrode, the auxiliary electrode was a platinum wire, and the reference electrode was a silver wire in contact with saturated tetrabutylammonium iodide, TBAI, in DMF. This electrode was checked for potential drifting before and after each reduction. No appreciable drift was observed. During the reductions, a maximum scan of 1.0 V with increments of 3 to 5 mV was applied. Two or three drops were averaged electronically for every point which was obtained in each polarographic scan. The measured potentials were corrected with respect to a mercury pool as reference electrode by adding -0.051 V to the experimental readings.

Ultraviolet spectra

UV spectra were obtained with a Cary 14 spectrophotometer at approximately 25°. The solvent was heptane (Spectroquality Grade, Matheson, Coleman and Bell). One centimeter quartz cells were employed in all cases except for 4,4′-bis(4-phenylbenzyl)biphenyl, which is extremely insoluble and which was observed in a 10 cm long cylindrical cell (2.7 cm diameter). The solutions of the biphenylyls were 1.0×10^{-5} *M* with the exception of the saturated solution of 4,4′-bis(4-phenylbenzyl)biphenyl in heptane.

Bis(4-biphenylyl)methane

This compound, apparently previously unreported, was synthesized by the method of Galun, Kalusyner, and Bergmann[14]. Biphenyl (0.2 mol) was mixed with 0.1 mol of chloral hydrate and warmed to 50° in a 500 ml three-necked flask equipped with a mechanical stirrer and a dropping funnel. Concentrated sulfuric acid (100 ml) was slowly added, and the mixture underwent the following changes in color: first blue, then yellow, pink, violet, dark brown, and finally yellow-brown. The temperature was held at 70° with an oil bath for 2 h. The reaction mixture was then poured into $1-1\frac{1}{2}$ kg of ice. The solid was filtered, and the water layer extracted with ether. Recrystallization from acetone of the recovered solid gave a very light yellow-green compound (I), which melted at 145°. The yield of this intermediate, $(C_6H_5C_6H_4)_2CHCCl_3$, was 60%. Potassium hydroxide (15.0 g) was dissolved in water (15 ml) and added to diethylene glycol (120 ml). Water was distilled from this solution until the temperature reached 180°. The solution was cooled to 100°, and 7.0 g of (I) was added. The reaction mixture was refluxed for $3-3\frac{1}{2}$ h. [Shorter periods of decarboxylation lead to the production of $(C_6H_5C_6H_4)_2C{=}CCl_2$.] Slow evolution of CO_2 was confirmed with a solution of $Ba(OH)_2$. After this reflux period, the mixture was poured onto crushed ice and allowed to stand overnight. The solid was filtered, the water layer extracted with ether, and the recovered solid was recrystallized from acetone to give a white product; m.p. 160–162°. Further recrystallizations from ethanol gave crystals with the same melting point. For this product and for other biphenylyls below, the sharpness of the NMR peaks due to methylene groups and the constancy of the melting points with recrystallization was taken as evidence for the purity of the *para* isomers. NMR (CCl_4, ref. TMS): δ 7.35 multiplet, δ 4.0 s, intensities, 18/2. (Found: C, 94.10; H, 6.23. $C_{25}H_{20}$ calcd.: C, 93.73; H, 6.27%.)

4,4′-Bis(4-phenylbenzyl)biphenyl

This compound was prepared by a Friedel–Crafts reaction of biphenyl and α,α-dihydroxobitolyl. First, α,α-dichlorobitolyl was prepared by a method described[15] for the synthesis of benzyl chloride. Biphenyl (15.4 g) was triturated with 40.0 g of anhydrous zinc chloride and transferred to a 250 ml, three-necked flask equipped with a mechanical stirrer, dropping funnel and condenser. Formalin (30 ml, 40% solution) was added. The mixture was warmed to 70–80° for 3 h while hydrogen chloride was bubbled into it. The solid was washed with water and dissolved in ether; the ethereal solution was washed with water, dilute sodium bicarbonate and again with water. The solution was dried (Na_2SO_4) and the ether was removed. The solid product melts at 130–132° after two recrystallizations from ethanol (lit.[16] 137°). NMR: δ 7.35 (singlet), δ 4.50 (singlet), intensities 2/1 35% yield.

Next α,α-dihydroxobitolyl was prepared from the organic chloride (6.0 g) and a solution of 6.0 g KOH in 200 ml of water. The mixture was refluxed for 12 h. The white product after recrystallization from ethanol melted at 188° (lit.[17] 190°). For the preparation of 4,4'-bis(4-phenylbenzyl)biphenyl, the alcohol (10 mmol) was triturated with 20 mmol of biphenyl, transferred to a 100 ml two-necked flask equipped with stirrer and dropping funnel, and then warmed to 50°. Concentrated sulfuric acid (20 ml) was added slowly while the mixture was stirred. The temperature was kept at 70° for $1–1\frac{1}{2}$ h, after which the contents of the flask were poured onto crushed ice and a gray, sand-like solid was obtained. This solid was extracted with hot ethanol and then treated with hot benzene from which a white solid was precipitated upon addition of ethanol to the solution. The product was recrystallized four times from benzene/ethanol and then chromatographed through a silica gel column (Silica gel grade 950, mesh 60–200, Dow Chemical Corporation) using 3/1 hexane/benzene. The white solid from this chromatographic separation was redissolved in benzene and precipitated with ethanol; m.p. 235°. NMR (CS_2): δ 7.50 multiplet, δ 4.17 s, intensities 26/4. (Found: C, 93.21; H, 6.15. $C_{38}H_{30}$ calcd.: C, 93.79; H, 6.21%.)

Bis(4-biphenylyl)dimethylsilane

4-Bromobiphenyl (0.1 mol in 200 ml ether) was allowed to react with n-butyllithium (0.12 mol, 60 ml hexane, 50 ml ethyl ether) at 0 to −5°. The reaction mixture was refluxed for 1 h; dimethyldichlorosilane (0.7 mol in 30 ml ether) was added, and the mixture was stirred for 18 h at 25°. After the addition of dilute sulfuric acid (250 ml, 10%) the organic layer was separated, washed repeatedly with distilled water, and dried over anhydrous sodium sulfate. The solid left after pumping off the solvent was recrystallized three times from hexane to yield white crystals; m.p. 175–177°; NMR (CCl_4): δ 7.45 multiplet, δ 0.7 s, intensity ratio, 3/1. (Found: C, 85.53; H, 6.57. $C_{26}H_{24}Si$ calcd.: C, 85.67; H, 6.62%.)

4,4'-*Bis(4-biphenylyldimethylsilyl)biphenyl*

4-Lithiobiphenyl (~0.05 mol in 30 ml ethyl ether) was added to 0.078 mol $(CH_3)_2SiCl_2$ (0.078 mol in 30 ml ethyl ether) and the reaction mixture was stirred overnight at 25° under N_2. The precipitate was filtered off and the solution was distilled at 1 mmHg. The fraction collected at 107° solidified upon cooling and was recrystallized twice from ether to yield $C_6H_5C_6H_4Si(CH_3)_2Cl$; m.p. 60°; NMR: δ 7.45 multiplet, δ 0.45 s, intensities ~3/2. The yellow residue, which did not distill below 200°, was dissolved in ether, decolorized with charcoal and recrystallized from hexane. The resulting white solid was identical with an authentic sample of bis(4-biphenylyl)dimethylsilane.

4,4'-Dilithiobiphenyl (~0.01 mol in 50 ml ether), prepared by the techniques described above for the reaction 4-bromobiphenyl and n-butyllithium, was added slowly to $C_6H_5C_6H_4Si(CH_3)_2Cl$ (0.0204 mol in 40 ml ether). The mixture was refluxed overnight under N_2, and then treated with dilute sulfuric acid. The organic layer was separated, washed with water several times and dried. The solvent was evaporated at reduced pressure and the solid was washed twice with boiling ether, dissolved in a mixture of hexane/benzene, passed through charcoal and allowed to crystallize. Two recrystallizations afforded a white product, with a m.p. of 175–177° and an NMR spectrum consisting of a complex multiplet centered around δ 7.35 and a singlet at δ 0.42 with integrated intensities of 26/12 as expected for $C_6H_5C_6H_4Si(CH_3)_2C_6H_4C_6H_4$-$Si(CH_3)_2C_6H_4C_6H_5$. (Found: C, 83.83; H, 6.87. $C_{40}H_{38}Si_2$ calcd.: C, 83.57; H, 6.66%.)

Phenyltrimethylsilane, dimethyldiphenylsilane, triphenylsilane, 1,2-diphenyltetramethyldisilane and 1,3-diphenylhexamethyltrisilane were prepared in this laboratory by known procedures[18] and characterized by NMR, gas chromatography, and elemental analysis. Tetraphenylsilane (PCR, Inc.) was recrystallized thrice from THF; m.p. 238°. 1,2-Diphenylethane (Matheson, Coleman and Bell) was recrystallized twice from ethanol; m.p. 52°. Diphenylmethane (Eastman Organic Chemicals) was dried and distilled at 1 mmHg. 2,2-Diphenylpropane (Pfaltz and Bauer) was redistilled at 1 mmHg.

N,N-Dimethylformamide (Matheson, Coleman and Bell) was dried for 24 h over calcium hydride (Fisher Scientific) and then distilled twice over phthalic anhydride under nitrogen atmosphere at 21 mmHg (approximately 50°). Only the middle 50% was collected under nitrogen and kept in a refrigerator for a period of no longer than two weeks.

RESULTS

Polarography

The observed reduction potentials are presented in Table 1. For the first reduction step of most compounds, the results from fundamental and 2nd harmonic a.c. polarograms differed by less than 1 mV. Also tabulated are the potentials referred to the Hg pool electrode; an adjustment term, -0.051 V, was used to lead to -2.050 V for biphenyl and thus permit comparisons with earlier results[5,19–21].

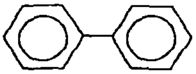
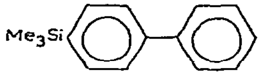
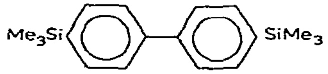
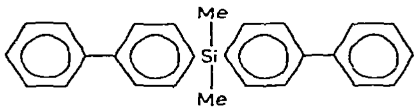
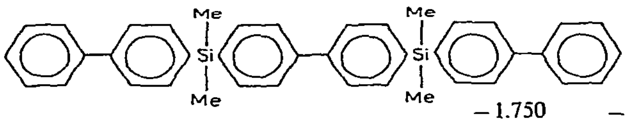
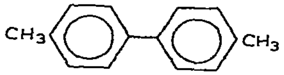
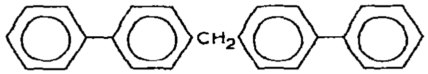
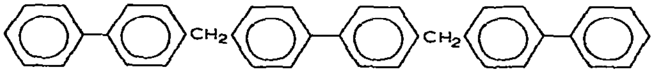
Reduction of the phenyl derivatives was observed neither under the same conditions used with the biphenylyls nor in solutions of THF/Bu_4NBF_4 or $THF/LiClO_4$. Apparently the supporting electrolyte is reduced at less negative potentials than the phenyl derivatives.

Four criteria for testing reversibility (or, Nernstian behavior) of the electron transfer step in these systems were applied:[22] (*i*) $E_{\frac{1}{2}}$ (d.c.) $= E_{\text{peak}}$ (a.c.); (*ii*) the width of the a.c. wave at half-height should be $90/n$ mV (n = number of electrons transferred); (*iii*) the potential at which the second harmonic wave goes to zero must be equal to $E_{\frac{1}{2}}$ (d.c.) and E_{peak} (a.c.); (*iv*) the separation between the maximum and the minimum of the second harmonic wave must be $0.068/n$ V for a reversible reduction. For the case where $n > 1$, these criteria assume that electron transfer proceeds via a single step, rather than by a sequence of successive steps. According to these criteria, the experimental results indicate that the first wave is the result of a reversible one-electron transfer in each compound investigated.

Second waves observed for bis(4-biphenylyl)methane and bis(4-biphenylyl)-

TABLE 1

POLAROGRAPHIC REDUCTION DATA FOR SUBSTITUTED BIPHENYLS

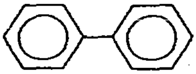
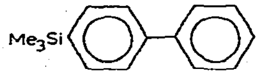
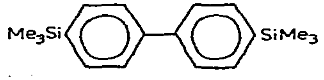
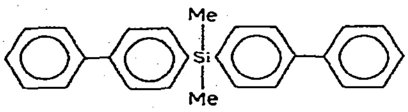
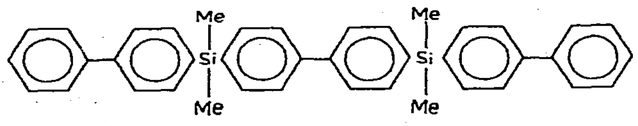
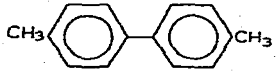
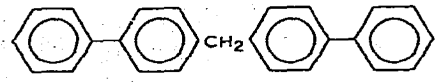
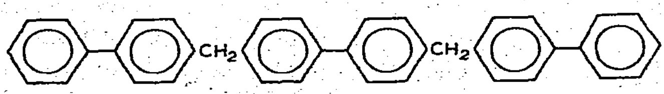
Compound	*1st wave Formal E^0 values (V)*[a]		*2nd wave Formal E^0 values (V)*[a]	
	Ag/TBAI	*"Hg pool"*	*Ag/TBAI*	*"Hg pool"*
	−1.999	−2.050		
	−1.897	−1.948		
	−1.805	−1.856		
	−1.853	−1.904	−2.010	−2.061
	−1.750	−1.801	−1.973 (2e)[c]	−2.024
		−2.194[b]		
	−2.019	−2.070	−2.133	−2.184
	−2.024	−2.075	−2.162 (2e)[c]	−2.213

[a] Evaluated from fundamental harmonic a.c. peak and second harmonic a.c. minimum potentials. [b] Ref. 21. [c] Two-electron step.

dimethylsilane also closely matched criteria for reversible one-electron transfer. On the other hand, second waves for 4,4′-bis(4-phenylbenzyl)biphenyl and 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl did not match the foregoing reversibility criteria and clearly involved the transfer of two electrons on the basis of the d.c. polarographic wave magnitudes. In the case of 4,4′-bis(4-phenylbenzyl)biphenyl, the a.c. polarographic data suggests that irreversibility is induced by rapid follow-up chemical decomposition of the di- and trianion products[22]. However, the fundamental and second harmonic a.c. polarographic responses at the second wave of 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl closely match theoretical predictions[23] for two successive, *reversible* one-electron transfer steps characterized by nearly identical

TABLE 2

ULTRAVIOLET DATA FOR SUBSTITUTED BIPHENYLS

Compound	*p-Band* λ_{max} *(nm)*	*Molar absorptivity* ($\times 10^{-3}$)
	247.1[a]	16.8
	255.0[a]	23.4
	262.2[a]	30.3
	258.8	55.6
	262.0	69.8
	254.8[b]	21.2
	257.4	40.4
	260.5	

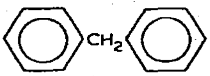
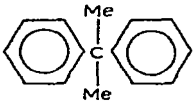
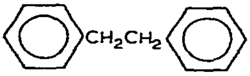
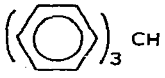
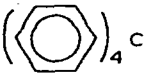
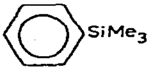
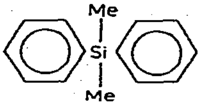
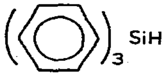
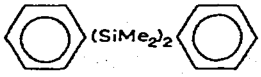
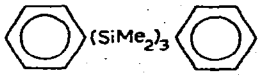
[a] Ref. 24. [b] Ref. 21.

E^0-values (see below). Only minor intervention of follow-up chemical decomposition is indicated in this case.

With the exception of a small irreversible third wave observed for bis(4-

TABLE 3

ULTRAVIOLET DATA FOR SUBSTITUTED BENZENES

Compound	*p-Band* λ_{max} *(nm)*	*α-Band*[a] λ_{max} *(nm)*
	206.0[b] 211.0 218.0	269.0[b]
	208.0[b]	269.7
	206.0[b] 210.0 215.0	268.0[b]
	199.0[b] 213.0 219.0	270.0[b]
	233.0[b]	272.0
	215.0 215.5 220.0	271.5
	216.5 221.0	271.8
	221.0 225.5	272.1
	221.0	273.5
	236.5	
	241.3	

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[a] Longest wavelength maximum. [b] Ref. 33; solvent:hexane.

biphenylyl)dimethylsilane, the a.c. polarographic peaks for successive reduction steps were better resolved for $C_6H_5C_6H_4SiMe_2C_6H_4C_6H_5$ and $C_6H_5C_6H_4SiMe_2C_6H_4$-$C_6H_4SiMe_2C_6H_4C_6H_5$ than for the methylene-bridged analogs.

Ultraviolet spectroscopy

Each biphenyl exhibited a broad, asymmetric *p*-band in the 257.0–263.0 nm region; maxima and intensities are presented in Table 2. For the phenyl derivatives, both α- and *p*-bands were observed and data are collected in Table 3. For each phenylsilane the *p*-band shows two shoulders in the region 215.0–221.0 nm. No maximum was observed for the *p*-band in any of the phenyl derivatives, and the wavelengths of the two shoulders are recorded for comparison purposes. The α-band in the 259.0–264.5 nm region displays fine structure. This band is present in all the hydrocarbons and in the phenylsilanes. In the case of the disilane and trisilane derivatives the α-band is not present; it may be submerged in the much stronger *p*-band.

DISCUSSION

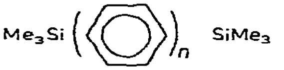
Polarography

All the biphenylsilanes are easier to reduce than biphenyl itself. This general difference is a consequence of the $(d\text{–}p)\pi$ and/or $(p\text{–}p)\pi$ bonding effect of the silicon atom with the π-orbitals of the aromatic system[5]. The π-bonding provides a way to delocalize electronic charge from the rings into the R_3Si-group making it easy to add an extra electron to the molecule. In other terms, the lowest empty molecular orbital lies at a lower energy than in biphenyl[5].

The methylene-bridged biphenyls are reduced at more negative potentials than biphenyl. In the case of the hydrocarbons two effects, inductive and hyperconjugative, may be playing substantial roles at the same time. Either an electron-releasing effect of methyl or methylene groups or a hyperconjugative effect should raise the energy of the lowest unoccupied molecular orbital making reduction more difficult[24].

A more detailed study of the biphenylsilanes shows an increasing change in the value of the reduction potentials towards less negative numbers with increasing number of silicon atoms substituted on the rings. Also a small shift in the same direction is observed when a $(C_6H_5C_6H_4)Me_2Si$-group is substituted for a Me_3Si-group.

However, the most important observation is that the differences in reduction potentials for the pairs 4-trimethylsilylbiphenyl and 4,4′-bis(trimethylsilyl)biphenyl; and bis(4-biphenylyl)dimethylsilane and 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl are essentially equal. From this fact it can be concluded that the difference in reduction potentials for the bridged organosilanes may be accounted for entirely by the effect of a second silicon atom, and thus there is no indication of the existence of a more extended conjugated system arising from a through conjugative effect of the *d* orbitals of the silicon atoms between the biphenyl entities. Further support for this hypothesis can be obtained from the observation of reduction potentials[20] for the series



($n = 1$ to 4)

where the difference in reduction potentials for the biphenyl and the terphenyl derivatives is 0.18 V and between the biphenyl and the quaterphenyl derivatives is 0.26 V, both appreciably higher than 0.103 V which is the difference of the potentials observed for the two dimethylsilyl-bridged biphenyls. Thus, increasing conjugation leads to less negative potentials and larger differences in reduction potentials within a series of polyphenyls than the ones observed for compounds containing silicon-bridged aromatic units and an equal or larger number of aromatic sub-units per molecule.

Electrochemical reduction at room temperature is possible for $Me_3SiC_6H_4$-$SiMe_3$ but not for $C_6H_5SiMe_2C_6H_5$.

The small shifts towards less negative potentials in the bridged compounds when compared with the mono- and bis-trimethylsilyl substituted biphenyls can be explained by invoking an inductive effect by the biphenyl units in the bridged compounds. Biphenyl is electronegative enough to stabilize the anion via an electron attractive inductive effect, if this effect can be transmitted through the silicon atom.

Since the electron density of the center aromatic unit in 4,4′-bis(biphenylyldimethylsilyl)biphenyl is decreased by two silicon atoms and by the two outer biphenyl rings, an added electron should preferentially go to the center unit. The next reduction step should take place in the outer biphenyl groups. The role of silicon acting either as a conjugative bridge or as an isolating group should markedly affect the potential for the second step. If the silicon atom behaves as an isolating group, the outer biphenyls should undergo reduction at almost the same potentials. If through conjugation were playing a dominant role, the effect of added charge should be important over the whole molecule, and the second and third electrons should be added at appreciably different potentials as a result of coulombic repulsions. The difference between the first and second reduction potential for each silane and hydrocarbon in Table 1 is small and roughly constant, consistent with negligible through conjugation.

Careful analysis of the a.c. response at the second wave of 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl using theoretical working curves (*e.g.*, Fig. 5 of ref. 23) indicates that the E^0-value for the third electron addition is only slightly more negative ($\approx 40 \pm 10$ mV) than the corresponding value for the second electron transfer. This result differs markedly from the 300–500 mV differences typically associated with E^0-values for successive electron transfers to highly-conjugated systems[25]. The latter observation again suggests the absence of significant through conjugation involving the silicon atom.

Similar trends are also present in the polarographic reduction of the hydrocarbons but here more than one effect producing the same results can be invoked. The UV spectra of 4-tert-butylbiphenyl and 4,4′-di-tert-butylbiphenyl have been interpreted[24] with a hyperconjugative model in which the tert-butyl group supplies a low-energy, filled orbital to the system. This filled orbital raises both the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals, with the rise more pronounced for the former. Theoretical arguments[26] predict more effective hyperconjugation for a methyl or methylene group than for a tert-butyl group. Consequently, the rise in energy of the LUMO in 4,4′-dimethylbiphenyl with respect to biphenyl as indicated by the more negative E^0 of the former compound can be rationalized in terms of hyperconjugation. Alternatively, these relative energies could be attributed to release of electrons by the methyl groups; however, some recent work suggests that methyl groups have the opposite inductive effect[27]. Whatever the effect which raises the LUMO energy, the differences in reduction potentials for 4,4′-dimethylbiphenyl, bis(4-biphenyl)methane, and 4,4′-bis(4-phenylbenzyl)biphenyl are too small to postulate significant through conjugation for the methylene bridge. Furthermore, increasing the conjugation in the system lowers the energy of the LUMO with respect to biphenyl as can be observed from the reduction potentials of biphenyl (2.05 V), terphenyl (1.80 V), quaterphenyl (1.67 V) *vs.* Hg pool[28]. In this series the differences in the reduction potentials between its members are considerably higher than the differences observed in the bridged hydrocarbons.

Ultraviolet spectroscopy

The maximum of the *p*-band for the $-SiMe_2-$ bridged biphenylyls is shifted only slightly with respect to the *p*-band position in the mono- and bis-trimethylsilylbiphenyl:

$$\lambda_{max}(C_6H_5C_6H_4SiMe_2C_6H_4C_6H_5) - \lambda_{max}(Me_3SiC_6H_4C_6H_5) = 3.8 \text{ nm}$$

$$\lambda_{max}[C_6H_5C_6H_4SiMe_2C_6H_4]_2 - \lambda_{max}Me_3SiC_6H_4C_6H_4SiMe_3 = 0.2 \text{ nm}$$

$$\lambda_{max}[C_6H_5C_6H_4SiMe_2C_6H_4]_2 - \lambda_{max}(C_6H_5C_6H_4SiMe_2C_6H_4C_6H_5) = 3.2 \text{ nm}$$

The smallness of the shift is more remarkable when it is compared with the differences in *p*-band positions of the members of the series biphenyl, terphenyl, quaterphenyl, and of the series $Me_3Si(C_6H_4)_nSiMe_3$ ($n = 2,3,4$). The absorption maxima for these compounds are listed in Table 4. In each of these series of compounds, the conjugated system is progressively extended by an additional ring providing a greater delocalization to the π-electrons. Concomitant with the enhanced delocalization, the energy difference between the highest occupied and the lowest unoccupied molecular orbitals becomes smaller and the absorption takes place at longer wavelengths. These observations of UV data are consistent with π-electron delocalization in the bridged compounds, silanes as well as hydrocarbons, not involving the entire molecule. The bridging groups appear to isolate the aromatic systems which are then individually excited[35]. The results also suggest that the excitation in 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl occurs mainly in the center unit since the wavelength for the absorption in this compound is the same as that of 4,4′-bis(trimethylsilyl)biphenyl. The outer rings in this compound, compared with methyl groups in $Me_3Si(C_6H_4)_2SiMe_3$, seem to play an inductive role. An inductive effect changes the energies

TABLE 4

ULTRAVIOLET SPECTRA OF $Y-(C_6H_4)_n-Y$

n	λ_{max} (*nm*)	
	$Y = H^a$	$Y = (CH_3)_3Si^b$
2	247.1	262.2
3	280.1	287.2
4	300.3	301.2

[a] Ref. 29. [b] Ref. 20.

of the HOMO and LUMO to the same extent so that no changes are predicted in the UV absorption[30]. This observation agrees with the results of polarographic measurements previously discussed.

For the phenylsilanes, the small differences within the p-band and α-band absorptions indicate that conjugation probably does not increase with the successive addition of phenyl rings to a silicon atom. The differences in absorption energies for some of the silanes compared with the analogous hydrocarbons are extremely small[31] and the fine structure observed in the α-band in the phenylsilanes resembles very closely that of benzene itself.

The slightly lower energies for the p-band transitions of the methylene-bridged biphenyls, relative to 4,4′-dimethylbiphenyl, may result from configuration interaction in the former compounds with which two transitions of the same symmetry type and similar energies are expected[32].

A completely different spectrum is obtained for $C_6H_5(SiMe_2)_nC_6H_5$, with $n =$ 2,3. A rather broad absorption without fine structure and shifted towards the red by about 15.0 nm from the p-band in the monosilanes is observed. Hague and Prince[18] have thoroughly discussed the absorption in $C_6H_5(SiMe_2)_2C_6H_5$ and assigned it to the C_6H_5–Si–Si entity. According to these authors an electron is promoted from a π-cloud of an aromatic ring, most probably from the highest occupied π-orbital, to the lowest empty π-orbital of the Si–Si group in which d orbitals of the silicon atom are involved. This model may be extended and applied when $n = 3$. In this particular case the π-orbital formed by the three silicon atoms lies at lower energies and the absorption is shifted to the red.

For the bisnaphthyl series, $Ar(SiMe_2)_nAr$, $n = 1$–3, the variation of the UV absorption maxima is minimal and the reduction potentials are constant within experimental error[34].

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35 *Note added in proof.* The slight increase of λ_{max} in the series $MeC_6H_4C_6H_4Me$, $(C_6H_5C_6H_4)_2CH_2$ and $(C_6H_5C_6H_4CH_2C_6H_4)_2$ is consistent with 1,3-interannular interactions. See J. D. Young, G. R. Stevenson and N. L. Bauld, *J. Amer. Chem. Soc.*, 94 (1972) 8790. No evidence for 1,3-interangular interactions across dimethylsilyl groups was obtained in the present investigation.