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DIMETHYLSILYL- AND METHYLENE-BRIDGED AROMATIC GROUPS

III. ELECTRON SPIN RESONANCE SPECTRA OF ANION RADICALS

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SUMMARY

From the ESR spectra of anion radicals of bis(4-biphenylyl)dimethylsilane and 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl, the delocalization of spin density is inferred. The bridging $-SiMe_2-$ groups separate practically independent π-systems. The rate of electron transfer between biphenyl sub-units is less than $\sim 10^6$ sec^{-1} at 223 K.

INTRODUCTION

Recently Kean, Fisher and West[1] reported the preparation of the anion radical of dimethyldiphenylsilane and the observations that at low temperature the unpaired electron is localized on one phenyl ring and with an increase in temperature the electron transfers rapidly between the rings. The ESR spectra of this anion radical and the anion radicals of $C_6H_5C_6H_4SiMe_2C_6H_4C_6H_5$, $C_6H_5C_6H_4SiMe_2C_6H_4C_6H_4$-$SiMe_2C_6H_4C_6H_5$, and $C_6H_5(SiMe_2)_{2,3}$ have been investigated independently in this laboratory. The purpose of this and previous[2,3] investigations was to determine if a $-SiMe_2-$ unit between aromatic rings participates in "through conjugation" or separates essentially independent π-systems.

EXPERIMENTAL

The compounds were prepared[2] and reduced[4] to anion radicals with alkali metal in THF near the melting point as reported previously. The biphenylyls were reduced with sodium and the benzenes with potassium, since their attempted reduction with sodium failed.

The ESR spectra were taken with a Bruker Scientific B-ER 418S spectrometer at X-band frequencies and with 100 kHz modulation. Most of the spectra were recorded at 223.0 ± 0.5 K. The microwave frequencies were obtained with a Model 535 PRD frequency meter. The value of the magnetic field, as measured with an NMR gaussmeter, and the corresponding signal intensity were simultaneously recorded on computer-compatible tape with a locally constructed digital data system[5]. ESR spectra were analyzed with either of two computer programs, SESRS[6] or DIZZY[5]. For the latter program, input data consists of the experimental spectrum and initial estimates of the linewidth and splitting constants for each set of equivalent nuclei. DIZZY by an iterative least-squares procedure calculates the splitting constants and linewidths which minimize the difference between the experimental and simulated spectra.

RESULTS AND DISCUSSION

Experimental and calculated spectra are presented in Figs. 1 to 5. For dimethyldiphenylsilane, spectra comparable to those reported previously[1] were observed. 1,2-Diphenyltetramethyldisilane and 1,3-diphenylhexamethyltrisilane behaved in a completely analogous way with each other upon reduction with potassium at low temperature and produced the same ESR spectra. Apparently the initially formed radicals decomposed and the products, depending upon conditions, included $[C_6H_5C_6H_5]^{\overline{\cdot}}$, $[C_6H_5SiMe_2C_6H_4SiMe_2C_6H_5]^{\overline{\cdot}}$ and a compound whose ESR spectrum was amazingly similar to that of naphthalene. $[C_6H_5SiMe_2C_6H_4SiMe_2C_6H_5]^{\overline{\cdot}}$

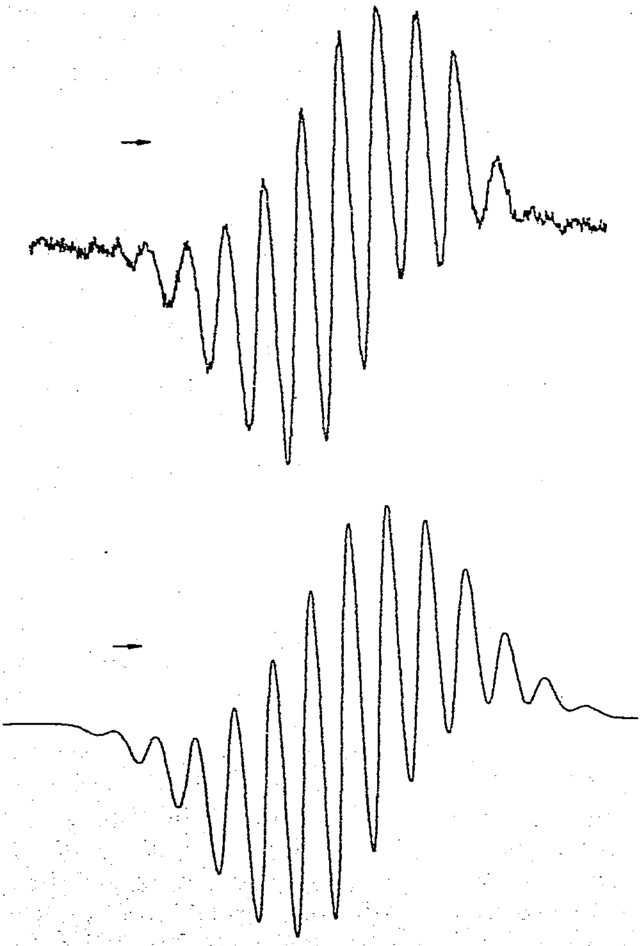


Fig. 1. ESR spectrum of the anion radical of 2,2-diphenylpropane in THF at 223 K. The computed spectrum is shown below the experimental spectrum, and the length of the arrow corresponds to 1G in each spectrum shown.

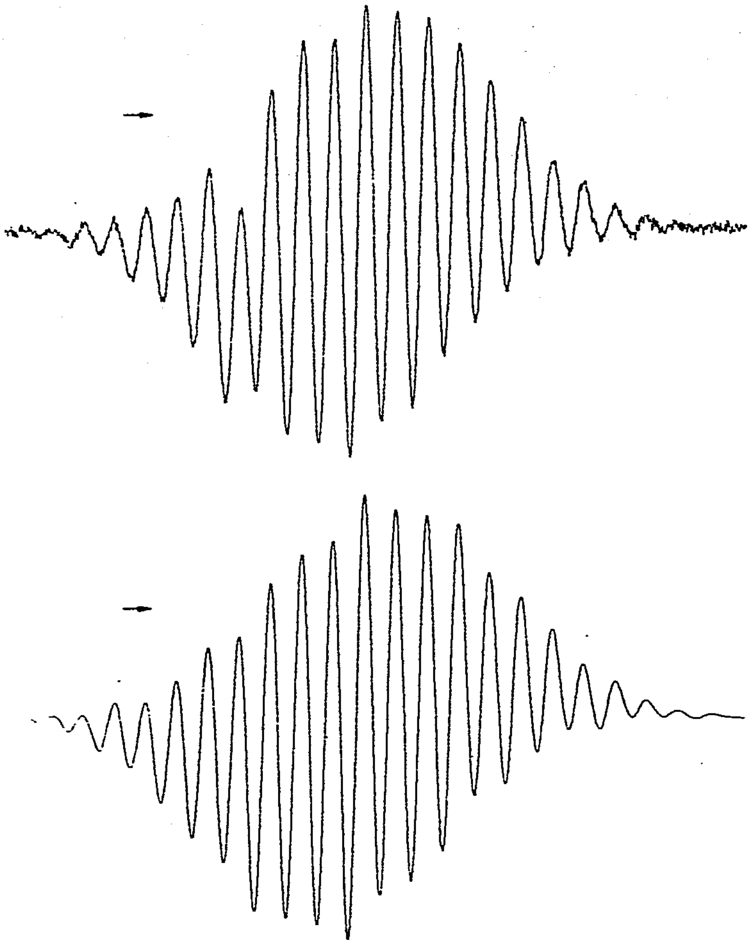


Fig. 2. Diphenylmethanide.

has been reported to be[1,7] a decomposition product of $[C_6H_5SiMe_2C_6H_5]^{\overline{\cdot}}$. Also, the methylene-bridged biphenyls, $C_6H_5C_6H_4CH_2C_6H_4C_6H_5$ and $(C_6H_5C_6H_4CH_2C_6H_4)_2$, reacted with sodium to give various anion-radical decomposition products.

The spectrum, Fig. 1, of the anion radical of 2,2-diphenylpropane was simulated with a linewidth of 0.28G and splitting constants of 2.649G for four *meta* (or *ortho*) protons, 1.375G for four *ortho* (or *meta*) protons, 0.176G for two *para* protons and 0.317G for six methyl protons. The latter two splittings were not resolved. These assignments are consistent with the rate of electron transfer between rings being $>10^8$ sec^{-1} [8]. The spectrum, Fig. 2, of the anion radical of diphenylmethane could not be fitted with the previously reported[9] splitting constants of 0.89G for two *para* protons and 2.23G for the remaining ten protons; this assignment was for the radical in dimethoxyethane at <203K. The simulated spectrum is based on a_i values of 3.24G (4H), 2.22G (4H), 0.216G (2 *para* H), and 1.15G (2 methylene H) and a linewidth of

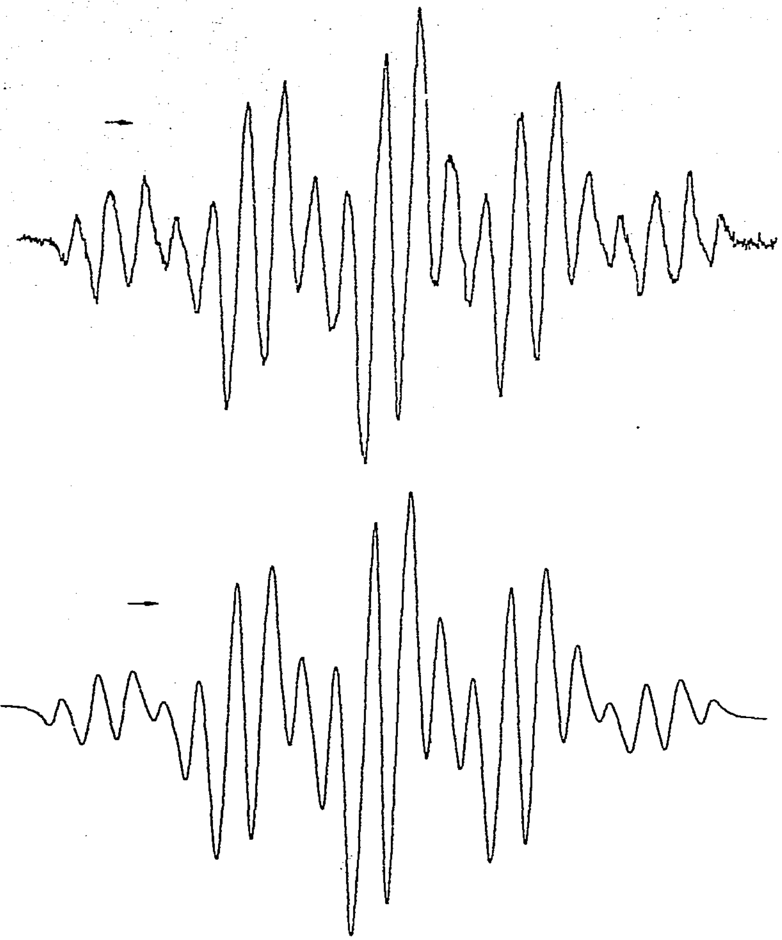


Fig. 3. 1,2-Diphenylethanide.

0.41G. The specific assignments of the latter two splitting constants follows from the observed a_i values for the anion radical of 2,2-diphenylpropane. Rapid electron transfer between rings in $[Ph_2CH_2]^{-}$ has been reported earlier[9,10]. The splitting constants for the anion radical of 1,2-diphenylethane, Fig. 3, are 4.79G (4H), 1.036G (1 *para* H) and 1.276G (2H) in agreement with those of Gerson and Martin[9] but not with those in ref. 11; thus the additional electron is localized on only one ring[9,10].

Bis(4-biphenylyl)dimethylsilane reacted with sodium to produce a green solution which exhibited the seven-peak ESR spectrum shown in Fig. 4 or sometimes a poorly resolved and unanalyzed eleven-line spectrum due to an apparent decomposition product. The former spectrum can be simulated closely with the splitting constants previously assigned[12] to $[Me_3SiC_6H_4C_6H_5]^{-}$ except for 0.20G instead of 0.16G for two ring protons and an a_{CH_3} value of 0.10G for six methyl protons instead of the previously observed 0.16G for nine methyl protons. The other splitting constants are 4.96 (*para*), 2.08 (2H), 2.72 (2H) and 0.48G (2H). The linewidth of approximately 0.27G

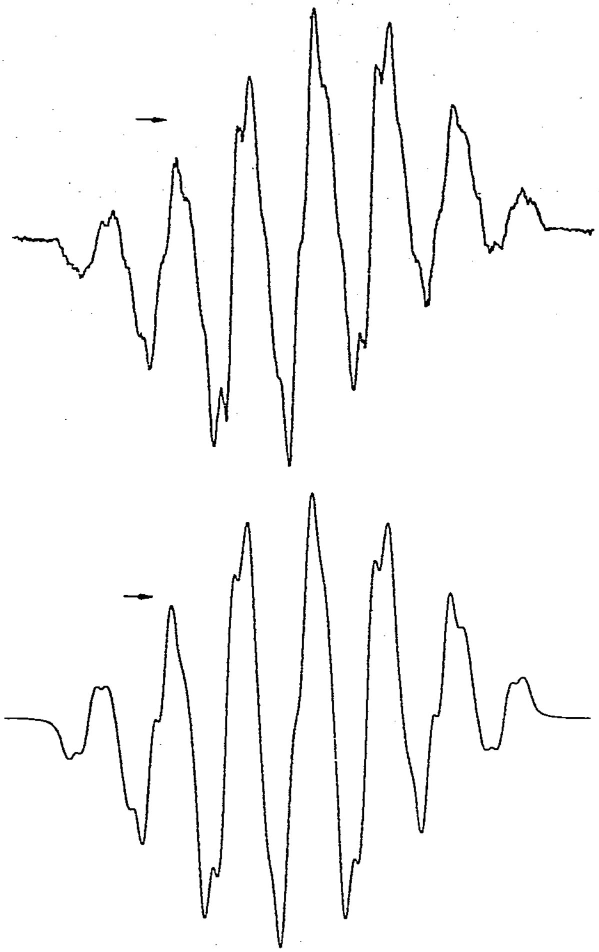


Fig. 4. Bis(4-biphenylyl)dimethylsilanide.

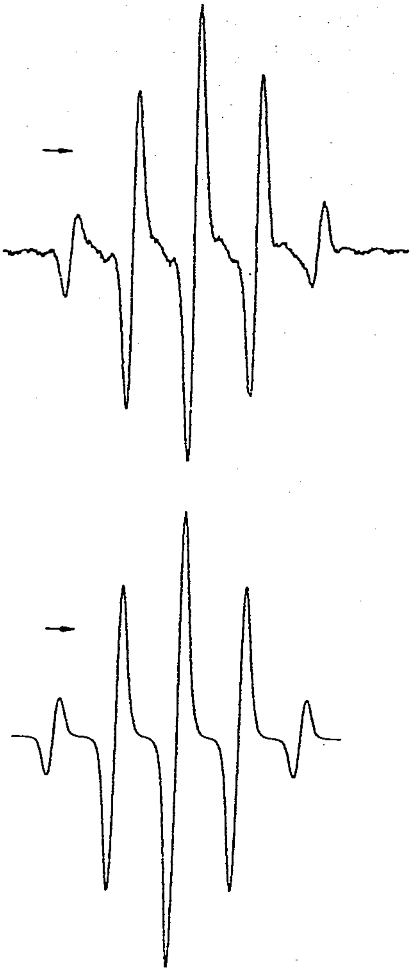


Fig. 5. 4,4'-Bis(4-biphenylyldimethylsilyl)biphenyl.

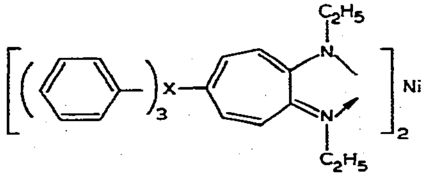
precluded observation of the hfs due to methyl protons. The radical being observed is definitely not $[Me_3SiC_6H_4C_6H_5]^{-}$ since successful spectral simulation would depend upon the a_i value for nine methyl hydrogens being less than 0.10G with any linewidth value. Therefore, the odd electron appears to be localized mainly in one biphenylyl unit and the rate of electron transfer is slow compared with the time scale of the ESR experiment. The rate of transfer seems to be slow in a wide range of temperature, since no changes were noticed in either hyperfine splitting or linewidths in the temperature range from 173 K to 273 K. When $C_6H_5C_6H_4SiMe_2C_6H_4C_6H_5$ was reduced with potassium, a spectrum very similar to that of the biphenyl radical anion was obtained.

4,4'-Bis(4-biphenylyldimethylsilyl)biphenyl also gave either of two ESR spectra upon reduction with sodium. For preparations giving green solutions, the ESR spectra consisted of seven broad, poorly-resolved peaks. Other preparations under rather similar conditions gave yellow solutions which exhibited spectra consisting of five peaks having relative intensities of 1/4/6/4/1 as shown in Fig. 5. The excellent calculated spectrum is based on a linewidth of 0.10G and splitting constants of 2.20G (4H), 0.14G (4H), and 0.06G (12H).

The experimental spectrum can also be simulated with linewidths increasing from 0.09G to 0.12G and a_{CH_3} (12H) decreasing from 0.07G to 0.04G with constant a_i values of 2.20G for 4H and 0.14G for 4H. For $[Me_3SiC_6H_4C_6H_4SiMe_3]^{\overline{\cdot}}$ the a_i values for ring protons are 2.24G and 0.14G but the a_i values for the eighteen methyl protons are 0.14G; the latter splittings were well resolved[12]. The results here are comparable to those above for bis(4-biphenylyl)dimethylsilane. The present spectrum could not be reproduced by assuming 2.20G (4H), 0.14G (4H) and a_i values larger than 0.05G for eighteen (methyl) protons. Thus the anion radical of 4,4′-bis(trimethylsilyl)-biphenyl, a conceivable decomposition product, is not responsible for the ESR spectrum in Fig. 5. Probably, the species responsible for the ESR spectrum is the anion-radical of the parent silane in which the unpaired electron resides mostly in the central aromatic unit. Polarography and ultraviolet spectroscopic data[2] are consistent with the central unit having a greater affinity for an extra electron. With the central unit, *two* silicon atoms would be involved in delocalization and stabilization of π electrons.

According to McConnell[13], an additional charge on 1,2-diphenylethane will tend to be stabilized on one ring relative to the other because of changes in nuclear configuration and solvent orientation. Comparable changes should tend to trap the charge in the above dimethylsilyl-bridged biphenyls. The rate of intramolecular electron transfer between rings is less in the $-SiMe_2$-bridged biphenyls than in the anion radical of $(C_6H_5)_2SiMe_2$[1]. The absence of a variation of the ESR spectra of the former compounds with temperature can be attributed to more stabilization from changes in solvent orientation and nuclear configuration with biphenyls than with the smaller phenyls.

In summary, silicon does not act to provide significant through-conjugation for the bridged biphenyls. This conclusion is consistent with the theoretical analysis by Jaffé[14] of through conjugation at tetrahedral atoms and of the observations[15] of the NMR spectra of



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