*Journal of Organometallic Chemistry*, 49 (1973) 365–371

# DIMETHYLSILYL- AND METHYLENE-BRIDGED AROMATIC GROUPS

## II. PHOSPHORESCENT TRIPLET STATES

FERNANDO CORREA-DURAN and A. L. ALLRED
*Department of Chemistry, Northwestern University, Evanston, Illinois* 60201 (*U.S.A.*)
(Received July 12th, 1972)

## SUMMARY

The zero-field splitting parameters *D* and *E*, or *D**, were measured by electron spin spectroscopy for the triplet states of bis(4-biphenylyl)dimethylsilane, 4,4′-bis(4-biphenylyldimethylsilyl)biphenyl, 1,2-diphenyltetramethyldisilane, several monosilanes, bis(4-biphenylyl)methane, 4,4′-bis(4-phenylbenzyl)biphenyl, and dimethyldiphenylmethane. The zero-field splitting values of compounds having biphenyl subunits bridged with either $-SiMe_2-$ or $-CH_2-$groups, compared with those of mono- and disubstituted biphenyls, show that the triplet electrons are localized mainly on one biphenyl group in each of the bridged compounds on the time scale of the ESR observations.

## INTRODUCTION

The extent to which silicon bonded between two aromatic groups can expand the conjugated system and thereby allow delocalization of $\pi$ electrons over the separated rings was studied recently[1] by polarography and electronic spectroscopy. The possibility of "through conjugation" by silicon has important implications for investigations referenced elsewhere[1].

The zero-field splitting (ZFS) parameter *D* in triplet state spectroscopy measures the interaction energy of the two spins. *D* is proportional to the average of the inverse cube of the interelectronic separation $\langle 1/r_{12}^3 \rangle$ and thus reflects the spatial distribution of the triplet electrons. As the region available to the two electrons increases, the interaction is less and *D* becomes smaller. The ZFS parameters of dimethylsilyl- and methylene-bridged phenyls and biphenyls will be compared herein with those of methyl- and trimethylsilyl-substituted benzenes and biphenyls to determine if the triplet exciton is delocalized over the whole molecule or is confined to only one of the bridged aromatic centers.

## EXPERIMENTAL

Bruker Scientific B-ER 418s and Varian E4 ESR spectrometers were used to record the triplet state spectra of the biphenyls and phenyls, respectively. The spectrometers were operated at X-band frequencies with the microwave field perpendicular to the external field and with 100 kHz modulation. High microwave and modulation power were necessary for the observation of most of the peaks. With the Bruker spectrometer, frequencies were obtained with a Model 535 PRD Electronics, Inc., meter and field values were obtained with a gaussmeter having an accuracy of ±0.01 gauss in the range 2400–4600 gauss. Below 2400 gauss field measurements were based on the observed linearity of the field.

Syntheses or commercial sources are given elsewhere[1].

The substituted biphenyls were dissolved (~0.1 *M*) in 2-methyltetrahydrofuran (Aldrich) and biphenyl and phenyl derivatives were dissolved (~0.1 *M*) in EPA (Matheson, Coleman and Bell; 5/5/2 solution of ethyl ether, isopentane and ethyl alcohol). The samples, contained in 4 mm o.d. quartz tubes and immersed in liquid $N_2$ in a quartz Dewar, were irradiated with a Hanovia 200 watt, high pressure Hg–Xe lamp equipped with a water filter.

## RESULTS

The intensities of the triplet state spectra of the randomly oriented triplets were weak. All six transitions in the $\Delta m = 1$ region were observed for trimethylsilylbenzene and for the biphenyls except for $(C_6H_5C_6H_4YC_6H_4)_2$ where $Y = CH_2$ or $SiMe_2$. For these two compounds, spectral analysis is based on the four observed transitions. A typical spectrum is reproduced in Fig. 1.

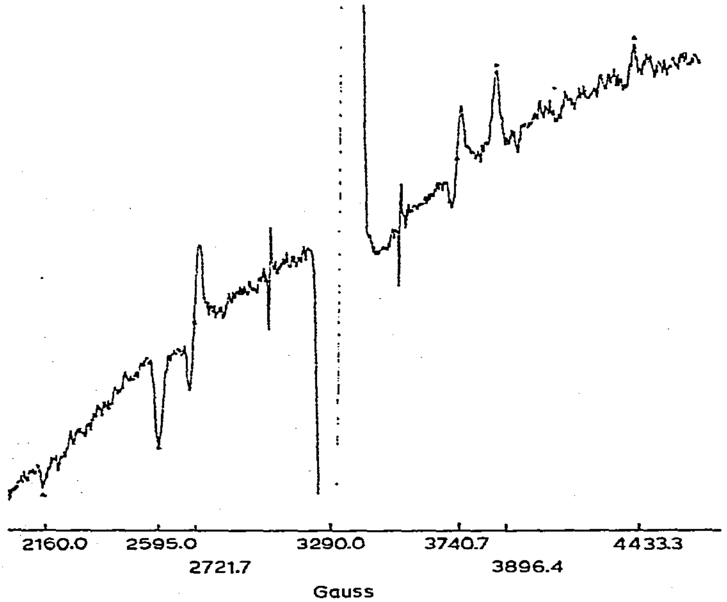


Fig. 1. The triplet state ESR spectrum in the $\Delta m = \pm 1$ region of bis(4-biphenylyl)methane in 2-methyltetrahydrofuran at 77 K.

The principal values, *X*, *Y*, and *Z*, of the zero-field splitting tensor were calculated from appropriate combinations of the equations[2]:

$$
\begin{aligned}
H_{x2} &= (2g_{xx}\cdot\beta)^{-1}[(2h\cdot\nu-3|X|)^2-(Y-Z)^2]^{\frac{1}{2}}\\
H_{x3} &= (2g_{xx}\cdot\beta)^{-1}[(2h\cdot\nu+3|X|)^2-(Y-Z)^2]^{\frac{1}{2}}
\end{aligned}
\tag*{(1)*}
$$

using 2.0023 as the initial value of $g_{xx}$, $g_{yy}$ and $g_{zz}$. Initial values for the ZFS parameters $D$ and $E$ were obtained from the relationships $D=-3Z/2$ and $E=-(X-Y)/2$.

Next $g_{xx}$, $g_{yy}$ and $g_{zz}$ were calculated from the equations[3]:

$$
\begin{aligned}
g_{xx} &= \left\{\frac{g\cdot e^2\cdot[2(h\cdot\nu)^2-4E\cdot(D-E)]}{H_{x2}^2+H_{x3}^2}\right\}^{\frac{1}{2}}\\
g_{yy} &= \left\{\frac{g\cdot e^2\cdot[2(h\cdot\nu)^2+4E\cdot(D+E)]}{H_{y2}^2+H_{y3}^2}\right\}^{\frac{1}{2}}\\
g_{zz} &= \left\{\frac{g\cdot e^2\cdot[(h\cdot\nu+D)^2+(h\cdot\nu-D)^2-2E^2]}{H_{z2}^2+H_{z3}^2}\right\}^{\frac{1}{2}}
\end{aligned}
\tag{2}
$$

and an iterative calculation involving eqns. (1) and (2) was made with a CDC 6400 computer to obtain self-consistent results for $X$, $Y$, $Z$, $g_{xx}$, $g_{yy}$ and $g_{zz}$. All calculated $g$ values were close to the $g$ value of the free electron and are isotropic within experimental accuracy. The final values of $D$ and $E$ are presented in Table 1.

For spectra in which the $\Delta m=\pm 1$ region did not show structure or in which a precise evaluation of the fields in this region was difficult due to irregularly shaped peaks, the ZFS parameter $D^*$ (equal to $[D^2+3E^2]^{\frac{1}{2}}$) was calculated from the $\Delta m=\pm 2$ transition and eqn. (3)

$$
D^* = \sqrt{3}\left[\tfrac{1}{4}(h\cdot\nu)^2-(g\cdot\beta\cdot H_{\min})^2\right]^{\frac{1}{2}}
\tag{3}
$$

with $g=2.0023$. $D^*$ values are presented in Table 2.

## DISCUSSION

The substitution of silyl groups led to smaller $D$ values which reflect a greater separation of the triplet electrons presumably as a consequence of greater delocalization of $\pi$-electron spin density. Low values of $D$ for organosilanes have been explained previously[4] in terms of $\pi$-bonding between silicon and contiguous aromatic rings. Comparison of $D$ values of trimethylsilylbenzene and biphenyl shows that the $Me_3Si$- and $C_6H_5$-groups produce comparable changes in $D$. The ability of the $Me_3Si$-group to delocalize $\pi$-electron density has been inferred from the ESR spectra of anion radicals[7,8].

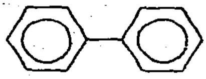
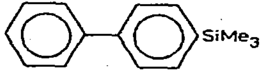
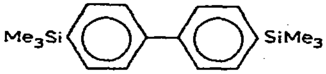
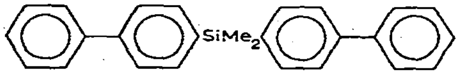
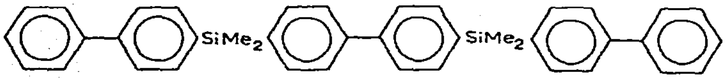
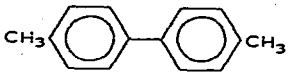
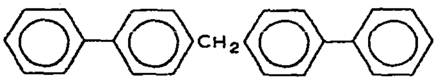
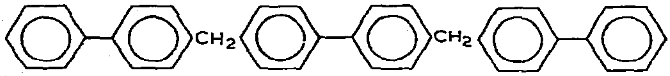
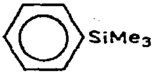
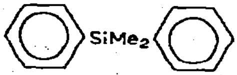
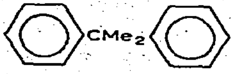
A comparison of $D$ values for dimethyldiphenylsilane with phenyltrimethylsilane, bis(4-biphenylyl)dimethylsilane with 4-trimethylsilylbiphenyl, 4,4'-bis(4-phenylbenzyl)biphenyl with 4,4'-dimethylbiphenyl, and 4,4'-bis(4-biphenylyldimethylsilyl)biphenyl with 4,4'-bis(trimethylsilyl)biphenyl shows that the values for each pair do not differ within experimental error, except for a slight difference within the last pair. In other words, the $-CH_2-$ and $-Me_2Si$-groups do not act as effective $\pi$-electron bridges between aromatic systems but rather tend to be isolating units. The inability of the empty $d$ orbitals on the silicon atom to provide significant

---

[*] Equations for $H_{y2}$, $H_{y3}$, $H_{z2}$, and $H_{z3}$ are obtainable by cyclic permutations of $X$, $Y$, and $Z$.

TABLE 1

ZFS PARAMETERS FOR SUBSTITUTED BIPHENYLS AND BENZENES

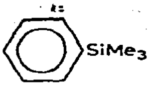
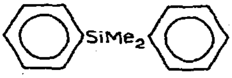
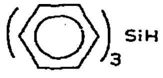
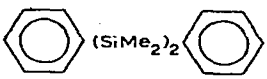
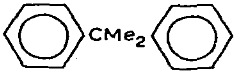
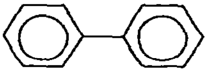
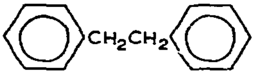
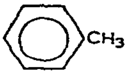
| *Compound* | $D(cm^{-1})^a$ | $E(cm^{-1})^a$ |
|---|---|---|
|  | 0.1093 | 0.0036 |
|  | 0.1051[b] | 0.0051[b] |
|  | 0.1024[b] | 0.0063[b] |
|  | 0.1049 | 0.0052 |
|  | 0.1014 | 0.0065 |
|  | 0.1054[b] | 0.0040[b] |
|  | 0.1066 | 0.0043 |
|  | 0.1057 | 0.0042 |
|  | 0.1092 | 0.0036 |
|  | 0.1092[c] | |
|  | 0.0938 | 0.0133 |
|  | 0.1581[d] | 0.0064[d] |

---

[a] The average deviation for 2 to 5 samples of each compound was $< 0.0003$ cm$^{-1}$ for $D$ and $< 0.0001$ cm$^{-1}$ for $E$. [b] Ref. 4. [c] Only $H_{zz}$ and $H_{z}$, were used for analysis. [d] Ref. 5.

TABLE 2.

ZFS PARAMETER $D^*$ OBTAINED FROM THE $\Delta m = \pm 2$ TRANSITION

| *Compound* | $D^*$ ($cm^{-1}$) |
|---|---|
|  | 0.1104 |
|  | 0.1099 |
|  | 0.1094 |
|  | 0.1073 |
|  | 0.0983 |
|  | 0.1103 |
|  | 0.1690 |
|  | 0.171[a] |

[a] Ref. 6; ethanol glass.

through-conjugation is apparent. Delocalization of the triplet state electrons is observed into but not through the group. The similarity of the $E$ values within each of the above pairs of compounds reflects comparable in-plane anisotropy of the triplet in the bridged and non-bridged molecules and is thus consistent with the absence of significant through-conjugation. Similar $E$ values for the above pairs should result if the triplet exciton is localized in part of each bridged molecule instead of on the whole molecule. The close similarity of the $D$ and $E$ values for the molecules containing two bridges and the corresponding 4,4′-disubstituted biphenyls suggest that the triplet electrons are confined mostly in a molecular orbital mainly localized in the central aromatic system.

Additional support for the hypothesis of no significant through-conjugation can be obtained from the triplet spectrum of triphenylsilane. The broad features around 2600 G and 3800 G can be interpreted as arising from two different peaks ($x$ and $y$ transitions) too close together to be fully resolved. The lack of coincidence of $X$ and $Y$ indicates that the triplet species does not possess threefold symmetry as should be the case if the triplet exciton were delocalized through the whole undistorted molecule. Due to the broadness of the peaks in the $\Delta m = \pm 1$ region, a precise estimation of the field values is difficult and the $H_{min}$ transition was chosen to evaluate $D^*$. The value of $D^*$, 0.1094 $cm^{-1}$, is very close to the $D^*$ values obtained for phenyltrimethylsilane and dimethyldiphenylsilane. This result indicates that the triplet exciton is not delocalized over the three rings of the molecule but rather is confined to a system involving one ring and the silicon atom. The triplet state spectrum of bis(2,2'-biphenylene)silane is consistent with either no exciton transfer occurring or a departure from axial symmetry in the temperature range 4.2 K to 200 K[9].

The low value of $D^*$ for 1,2-diphenyltetramethyldisilane is an indication that the second silicon atom adds to some extent to the conjugated system formed by the phenyl ring and the first silicon atom. It is interesting to point out that phosphorescence life-times decrease rapidly with the successive addition of silicon atoms; for 1,3-diphenylhexamethyltrisilane, no afterglow is observed. A triplet state of the latter compound could not be detected by ESR.

The decrease in the value of $D$ of the methyl-substituted or methylene-bridged biphenyls with respect to biphenyl itself indicates that those groups are involved in $\pi$-electron spin delocalization although through-conjugation is unlikely. Assuming hyperconjugation as a probable mechanism by which the methyl group or methylene group are integrated into the conjugated system, it is reasonable that the rotation of the two aromatic rings at each side of the $-CH_2$-bridge inhibits through-conjugation to some extent. ESR spectra of methyl-substituted aromatic anion radicals indicate that $\pi$-electron spin density is transferred to the methyl groups mainly by a hyperconjugative effect[10,11].

No phosphorescence was observed for tert-butylbenzene and diphenylmethane. Phosphorescence is observed for 1,2-diphenylethane and 2,2-diphenylpropane. The low value of $D$ for 2,2-diphenylpropane is consistent with either (*a*) delocalization of spin density over one ring and the $-C(CH_3)_2$-group, or (*b*) the methyl groups on the carbon bridge sterically hindering the free rotation of the rings and causing a conformation that is favorable for hyperconjugation involving the bridge and both rings[13]. This latter possibility is supported by Corey–Pauling–Koltun molecular models.

The $D^*$ parameter for 1,2-diphenylethane is very close to the $D^*$ of toluene, implying that the triplet electrons are localized on half of the molecule. This result was also obtained[12] from the ESR spectrum of the anion radical of the compound, and is one more indication that triplet state spectroscopy is a valuable tool in describing $\pi$-electron delocalization in conjugated systems.

## ACKNOWLEDGEMENTS

F. Correa-Duran expresses appreciation to the Ford Foundation and to the Rockefeller Foundation for Fellowships, and to B. M. Hoffman for helpful discussions.

## REFERENCES

1 F. Correa-Duran, A. L. Allred, D. E. Glover and D. E. Smith, *J. Organometal. Chem.*, 49 (1973) 353.
2 P. Kottis and R. Lefebvre, *J. Chem. Phys.*, 41 (1963) 379.
3 E. Wasserman, L. C. Snyder and W. A. Yager, *J. Chem. Phys.*, 41 (1964) 1763.
4 H. V. Taylor, A. L. Allred and B. M. Hoffman, *J. Amer. Chem. Soc.*, 94 (1972) in press.
5 M. S. de Groot, J. H. Van der Waals and I. A. M. Hesselmann, *Mol. Phys.*, 16 (1969) 45.
6 M. S. de Groot and J. H. Van der Waals, *Mol. Phys.*, 6 (1962) 545.
7 J. A. Bedford, J. R. Bolton, A. Carrington and R. H. Prince, *Trans. Faraday Soc.*, 59 (1963) 53.
8 M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, 87 (1965) 2554.
9 A. L. Shain, J. P. Ackerman and W. Teague, *Chem. Phys. Lett.*, 3 (1969) 550.
10 J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, 5 (1962) 31.
11 A. Valenzuela and A. J. Bard, *J. Phys. Chem.*, 73 (1969) 779.
12 F. Correa-Duran, A. L. Allred and R. J. Loyd, *J. Organometal. Chem.*, 49 (1973) 373.
13 *Note added in proof.* For 2,2-diphenylpropane, but not for either of the bridged biphenyls, the low value of $D$ and the high value of $E$ are consistent with a 1,3-interannular interaction which has been postulated to explain electron delocalization in certain *para*-substituted diphenylmethane anion radicals: J. D. Young, G. R. Stevenson and N. L. Bauld, *J. Amer. Chem. Soc.*, 94 (1972) 8790.