Our conclusion is that polymers may provide extremely useful ways for protecting anhydrous and pyrophoric reagents and attempts are underway to further explore the concept using other reactive reagents. The complete scope of Ⓟ-AlCl$_3$ reactions will be described in a full paper to be published on the work in the near future.

Table I. Product Ratios from the Reaction of Dicyclopropylcarbinol and Ⓟ-AlCl$_3$

% Al in copolymer[a]	Yield of ether,[b] %	% conversion[c]
0	0	0
0.57	74.5	33.1
1.83	64.5	56.8
2.20	58.5	66.5
Pure AlCl$_3$	48.0	75.0

[a] Aluminum analyses by atomic absorption. [b] Analyses after 30 min at 50°. [c] The remainder of the products under these conditions were dimeric and of higher molecular weight.

Table II. Ⓟ-AlCl$_3$ Reactions of Carbinols[a]

Carbinol	Solvent alcohol	Polymer (% Al)	% ether
Dicyclopropyl-carbinol	MeOH	0.57	90.4
	EtOH	0.57	65.0
	i-PrOH	0.57	42.5
	t-BuOH	0.57	19.0
Triphenylcarbinol	MeOH	2.20	81.5
	EtOH	2.20	83.0
Diphenylmethyl-carbinol	MeOH	2.20	75.8[b]
	EtOH	2.20	59.0[b]
	MeOH	0.57	93.0[b]
Phenyldimethyl-carbinol	MeOH	0.57	50.0
tert-Butyl alcohol	MeOH	0.57	0

[a] All reactions were carried out at 60 ± 5° for 90 min. [b] 1,1-Diphenylethylene is the other product.

Table III. Yield of Dicyclopropylcarbinyl Isopropyl Ether as a Function of Solvent Composition[a]

Solvent	Concn of solvent to isopropyl alcohol, wt:wt	Yield of dicyclopropylcarbinyl isopropyl ether, %	Carbinol remaining, %
Hexane	0	57.0	43.0
	1:3	50.1[b]	2.0
	1:1	76.5[b]	2.0
	3:1	80.6[b]	2.0
Benzene	0	57.0	43.0
	1:3	65.0[b]	2.1
	1:1	69.6[b]	1.8
	3:1	81.0[b]	2.0
Carbon disulfide	0	57.0[b]	43.0
	1:3	48.7[b]	2.0
	1:1	77.7[b]	1.7
	3:1	81.4[b]	2.0

[a] All experiments were conducted with polymer containing 0.57% Al. [b] The remainder of the product in these cases was the ring-opened ether.

Acknowledgment. The authors acknowledge the support of the Research Corportion and the National Science Foundation, Grant No. GP-33566, for this work. Helpful discussions with Professor Erich Blossey are also acknowledged.

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(10) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

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Received August 11, 1972

Electronic Spectra of 1,1,2,2-Tetramethyl-3,4-benzo-1,2-disilacyclopentene-3 and Related Compounds. Stereoelectronic Verification of σ–π Conjugation between Silicon–Silicon σ Bonds and Benzenoid π Systems

Sir:

In 1964 we,[1] Gilman, *et al.*,[2] and Hague and Prince[3] reported independently that the silicon–silicon bond has conjugating properties with phenyl and vinyl groups. Phenylpentamethyldisilane shows an intense absorption at 43,300 cm^{-1} (ϵ 10,900);[1] the introduction of a pentamethyldisilanyl group into benzene causes a red shift to the extent of 6000 cm^{-1} in the $^{1}L_a$ band, whereas the trimethylsilyl group has only a small bathochromic effect on benzene[4] or ethylene.[5] These "conjugating properties" have been rationalized at first in terms of "d–π^*" interaction in the excited state.[1–3,6–8] Later the ground-state interaction between the silicon–silicon σ bond and the π system has been recognized as an important factor in addition to d–π^* interactions. The σ–π interaction has been suggested from the results of uv[9] and charge-transfer[10] spectra. More recently, the photoelectron spectrum has demonstrated that the highest occupied molecular orbital of phenylpentamethyldisilane is a linear combination of σ(SiSi) and $\pi(C_6H_5)$ orbitals.[11] We have also indicated the considerable σ-donor character of the silicon–silicon bond in the study of substituent effects on electronic and charge-transfer spectra of phenylpentamethyldisilanes.[12] Currently, σ–π conjugation between the carbon–metal bonds and π systems in the cationic species has been well documented.[13]

In this paper, we show stereoelectronic evidence that provides a strong indication of σ–π conjugation between the silicon–silicon bond and the π system in determining the electronic properties of phenyldisilanes.

1,1,2,2-Tetramethyl-3,4-benzo-1,2-disilacyclopentene-

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(1) H. Sakurai and M. Kumada, *Bull. Chem. Soc. Jap.*, **37**, 1894 (1964).

(2) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.*, **2**, 369 (1964).

(3) D. N. Hague and R. H. Prince, *Chem. Ind. (London)*, 1492 (1964).

(4) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(5) C. E. Scott and C. C. Price, *J. Amer. Chem. Soc.*, **81**, 2670 (1959).

(6) D. N. Hague and R. H. Prince, *J. Chem. Soc.*, 4690 (1965).

(7) C. G. Pitt, L. L. Jones, and B. G. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5471 (1967).

(8) H. Sakurai, H. Yamamori, and M. Kumada, *Chem. Commun.*, 198 (1968).

(9) C. G. Pitt, *J. Amer. Chem. Soc.*, **91**, 6613 (1968).

(10) H. Bock and H. Alt, *ibid.*, **92**, 1569 (1970), have also suggested inductive polarization of the benzene molecular orbitals by the β-trimethylsilyl group in phenylpentamethyldisilane.

(11) C. G. Pitt and H. Bock, *Chem. Commun.*, 28 (1972).

(12) H. Sakurai and M. Kira, the 4th Symposium on Structural Organic Chemistry, Oct 1971, Sendai, Japan, Abstracts, p 94; manuscript to be published.

(13) T. G. Traylor, H. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), summarized the previous works on σ–π conjugation.

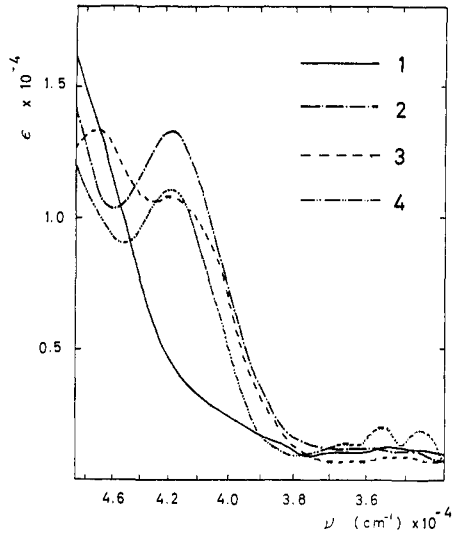
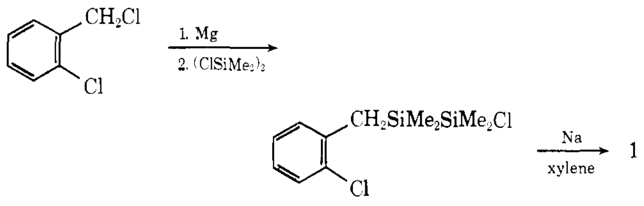


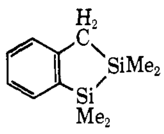
Figure 1. Electronic spectra of some organodisilanes in *n*-hexane.

3 (**1**) [bp 116–117° (25 mm); nmr (CCl$_4$) δ 0.22 (s, 6 H), 0.29 (s, 6 H), 2.23 (s, 2 H), 7.13 (m, 4 H); mass spectrum *m/e* 206 (M$^+$)] was prepared by the following sequence of reactions.

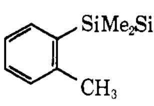


As reference compounds, *o*-methylphenylpentamethyldisilane (**2**) [bp 121° (20 mm); d_4^{20} 0.8878, n^{20}_{D} 1.5200; MR 76.18 (calcd, 75.72); nmr (CCl$_4$) δ 0.05 (s, 9 H), 0.36 (s, 6 H), 2.38 (s, 3 H), *ca.* 7.13 (m, 4 H); mass spectrum *m/e* 222 (M$^+$)], *o*-(trimethylsilyl)methylphenylpentamethyldisilane (**3**) [bp 106–146° (2 mm)[14]; nmr (CCl$_4$) δ −0.01 (s, 9 H), 0.00 (s, 9 H), 0.32 (s, 6 H), 2.16 (s, 2 H), 7.07 (m, 4 H); mass spectrum *m/e* 294 (M$^+$)], and 1-trimethylsilyl-1-methyl-2,3-benzo-1-silacyclopentene-2 (**4**) [bp 104° (6 mm); nmr (CCl$_4$) δ 0.00 (s, 9 H), 0.23 (s, 3 H), *ca.* 1.00 (m, 2 H), *ca.* 3.00 (m, 2 H), 7.19 (m, 4 H); mass spectrum *m/e* 220 (M$^+$)] were also prepared.[15]

Electronic spectra of these compounds in *n*-hexane are shown in Table I and summarized in Figure 1. Since both silicon–silicon and benzylic carbon–silicon bonds of **1** are in the nodal plane of the π system, no σ–π conjugation is possible in this compound. As a result, no intense ${}^{1}\mathrm{L}_{a}$ absorption corresponding to both benzylsilanes and phenyldisilanes should be observed for **1**. This prediction for **1** is verified by the absence of the characteristic ${}^{1}\mathrm{L}_{a}$ band of Ph–Si–Si at 43,000 cm^{-1} that is found in **2**, **3**, and **4**. Interestingly, two bands which may arise from both σ(CH$_2$Si) and σ(SiSi) bonds were observed for **3**, while a single intense absorption at 41,600 cm^{-1} (ϵ 21,100) was observed for *p*-(trimethylsilyl)methylphenylpentamethyldisilane (**5**).



1



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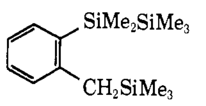

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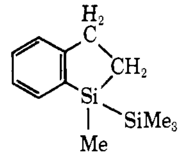

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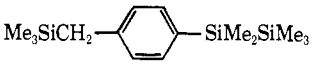

5

Table I. Frequencies of Electronic Spectra in *n*-Hexane

Compd	ν (${}^{1}\mathrm{L}_{a}$), cm^{-1}	ϵ
1	(End absorption)	
2	42,900	13,000
3	45,700	13,000
	42,900	10,700
4	42,900	11,000
5	41,600	21,100

These data demonstrate unequivocally the importance of σ–π conjugation with the silicon–silicon bond as well as with the carbon–silicon bond[16] in determining the electronic properties of the ground states.

Conjugation of the d–π^* type is also important since although benzyltrimethylsilane and phenylpentamethyldisilane have identical energies of the highest occupied molecular orbitals (8.35 eV),[11] the absorptions of the ${}^{1}\mathrm{L}_{a}$ bands differ considerably, the former occurring at higher energy (45,500 cm^{-1} (ϵ 8900)).

Traylor, *et al.*, have pointed out recently that σ–π conjugation will be much less effective if a conjugating sp^3 hybrid orbital belongs to a second or higher row element.[13] This may be generally valid, but if a metal–metal bond is linked with a π system, a lower ionization energy of the metal–metal bond makes the σ–π interaction better energetically than expected from the poor conjugating abilities of these elements as shown in this study. Further work is in progress and will be reported elsewhere.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

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Received April 18, 1972

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[14] This fraction contained three constituents, of which pure 3 was separated by means of preparative glc.

[15] Satisfactory elemental analyses were obtained for all new compounds.

[16] H. Sakurai, M. Kira, and M. Ochiai, *Chem. Lett.*, 87 (1972), have demonstrated a linear relationship between electronic transition and charge-transfer energies of various benzyl-group IV metals.