

Transmission of electronic effects via a SiMe_2 spacer in 4-mono- and 4,4'-disubstituted diphenyldimethylsilanes: ^{29}Si and ^{13}C NMR spectroscopy and PM3 semi-empirical calculations

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Abstract

Some ^{29}Si and ^{13}C NMR studies were performed on series of 4-substituted phenyltrimethylsilanes and 4-substituted and 4,4'-disubstituted diphenyldimethylsilanes. Within each series linear relationships are found between the chemical shifts and (a) the Hammett substituent constants σ_p and (b) the PM3-calculated total atomic charges. It is inferred that the SiMe_2 σ -type spacer weakly mediates substituent effects in the ground state via a bond polarization mechanism. A comparison with available data for 4-substituted and 4,4'-disubstituted diphenylmethanes shows that the SiMe_2 group is a better transmitter of electronic effects than the CH_2 group.

Keywords: Silicon; ^{29}Si NMR; ^{13}C NMR; Substituent effects; MO calculations

1. Introduction

In contrast with their carbon analogues, catenates of Group 14 metals exhibit interesting electronic properties. Oligo- and polysilylenes in particular have received considerable attention owing to their potential for application in optoelectronics [1]. The properties of these silane derivatives originate in the ease of electron delocalization [1], the presence of polarizable valence electrons [2] and σ - π interactions [3]. However, the ability of a single silicon atom to participate in π -conjugated systems (through σ - π conjugation) or to mediate electronic effects is not very clear. Information thought to favour σ - π participation of silicon has been derived from ESR spectroscopy on aryl-substituted silane anions [4–6], photoelectron spectroscopy (PES) [7] and ^1H - ^1H coupling constants [8] but, in contrast, UV [9], electrochemical [10], ESR [11,12] and PES [13] studies indicated that σ - π conjugation, if present, is only weak. Recently we found that photoinduced charge transfer occurs in donor-acceptor substituted diphenyldimethyl-

silanes [14], and this prompted us to investigate further possible ground-state interactions in such systems.

In this paper, the results of ^{29}Si and ^{13}C NMR studies on series of 4-substituted phenyltrimethylsilanes (**1a-i**), 4-substituted diphenyldimethylsilanes (**2a-i**) and 4,4'-disubstituted diphenyldimethylsilanes (**3a-i**) are reported and considered along with the results of PM3 semi-empirical calculations (Scheme 1, Table 1). Dimethylamino, methoxy and methylthio groups were used as electron donors, and bromo, cyano, dicyanoethenyl and methylsulphonyl groups as electron acceptors. Both the NMR data and the results of theoretical calculations show that the charge distribution in compounds **1-3a-i** is markedly affected by the substituent and provide insight into the ability of a single silicon atom to mediate electronic effects.

2. Experimental section

2.1. General

All reactions were conducted under nitrogen. Ethanol and DMF were stored over 4 Å and methanol over 3 Å molecular sieves prior to use. Other solvents were dis-

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tilled before use; diethyl ether was distilled from sodium–benzophenone. Starting materials and reagents were commercial products and used without further purification. Column chromatography was performed on silica (Merck Kieselgel 60, 230–400 mesh ASTM). NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR and 60 MHz for ^{29}Si NMR. The ^{29}Si NMR spectra were collected using a proton-decoupled inverse gated pulse sequence with a relaxation delay of 15 s.

Concentrations of ca. 0.05 M in CDCl_3 were used; solutions for ^{29}Si NMR spectroscopy contained 50 mM of chromium(III) acetylacetonate. Chemical shifts are given relative to external TMS for ^1H and ^{13}C NMR and internal TMS for ^{29}Si NMR.

Infrared spectra were measured on a Perkin-Elmer 283 spectrometer; solids were examined as KBr pellets and liquids between NaCl plates. GC–MS analyses were carried out with a Hewlett-Packard Model 5890 gas chromatograph linked to a JEOL JMS-AX505W mass spectrometer (70 eV EI). Melting points were determined on a Mettler FP5/FP51 photoelectric apparatus. Calculations were performed with the PM3 parametrization of the MNDO hamiltonian [15] as implemented in MOPAC 6.0 [16] on a 486/33 MHz personal computer. For the calculation on **3h** the MOPAC93 package available at the CAOS/CAMM centre at the University of Nijmegen, Netherlands, was used. Total atomic charges were extracted from fully optimized (precise option) structures. No symmetry constraints were imposed during the geometry optimizations.

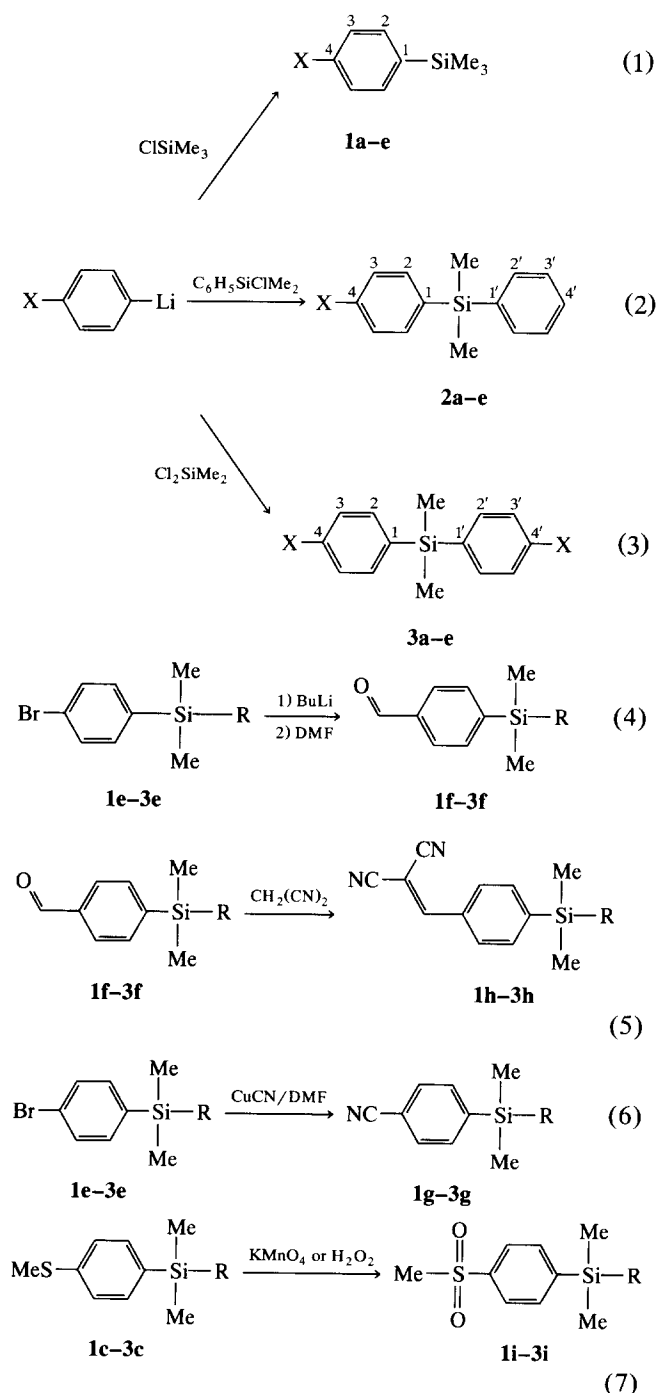
2.2. Syntheses

The syntheses of 4-trimethylsilyl-*N,N*-dimethylaniline (**1a**) [17], 4-trimethylsilylanisole (**1b**) [17], phenyltrimethylsilane (**1d**) [18], (4-bromophenyl)trimethylsilane (**1e**) [18] and diphenyldimethylsilane (**2d**) [19] have been described elsewhere. Only spectroscopic data are given for these compounds.

4-Substituted phenyltrimethylsilanes **1a–e**

Representative example 4-(trimethylsilyl)bromobenzene (1e). Chlorotrimethylsilane (14 ml, 110 mmol) was added to a solution of 4-bromophenyllithium (111 mmol) [20] in 150 ml of diethyl ether; a white solid formed immediately. The mixture was stirred overnight at room temperature, and 100 ml of 10% ammonium chloride solution was then added. The organic layer was separated, washed twice with 10% ammonium chloride solution, dried over magnesium sulphate and filtered. Volatile components were removed under reduced pressure and the liquid residue was distilled under reduced pressure (0.5 mmHg); the fraction boiling at 73–74°C was collected. Yield 19.71 g (86 mmol, 78%). ^1H NMR (ppm): δ 7.56, 7.45 (AA'BB', 2 $\times$ 2H, Ar–H); 0.34 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 139.2; 135.0; 131.0; 123.7; –1.2 (SiMe). IR (NaCl, cm^{-1}): ν 1256, 850–800 (Si–Me); 1115 (Si–Ar).

4-(Trimethylsilyl)-*N,N*-dimethylaniline (1a). ^1H NMR (ppm): δ 7.52, 6.86 (AA'XX', 2 $\times$ 2H, Ar–H); 3.05 (s, 6H, NMe); 0.36 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 151.1; 134.5; 125.7; 112.1; 40.4 (NMe); –0.7 (SiMe). IR (NaCl, cm^{-1}): ν 2790 (NMe₂); 1250, 850–800 (Si–Me); 1105 (Si–Ar).



Scheme 1.

4-(Trimethylsilyl)anisole (1b). ^1H NMR (ppm): δ 7.56, 7.01 (AA'XX', $2 \times 2\text{H}$, Ar-H); 3.89 (s, 3H, OMe); 0.36 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 160.4; 134.8; 131.4; 113.6; 55.0 (OMe); -0.8 (SiMe). IR (NaCl, cm^{-1}): ν 2820, 1270, 1030 (OMe); 1250, 850–800 (Si-Me); 1110 (Si-Ar).

4-(Trimethylsilyl)thioanisole (1c). Yield 9.29 g (47.3 mmol, 96%). The crude product, a pale yellow oil, was shown to be pure **1c**, m.p. 16°C . ^1H NMR (ppm): δ 7.50, 7.31 (AA'BB', $2 \times 2\text{H}$, Ar-H); 2.53 (s, 3H, SMe); 0.33 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 139.8; 136.4; 134.1; 126.0; 15.7 (SMe); -1.2 (SiMe). IR (NaCl, cm^{-1}): ν 1325 (SMe); 1250, 850–800 (Si-Me); 1090 (Si-Ar).

Phenyltrimethylsilane (1d). ^1H NMR (ppm): δ 7.58 (m, 2H, Ar-H); 7.39 (m, 3H, Ar-H); 0.32 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 140.5; 133.3; 128.8; 127.8; -1.1 (SiMe). IR (NaCl, cm^{-1}): ν 3060, 3045 (Ar-H); 1250, 830 (Si-Me); 1115 (Si-Ar).

4-Phenyl-substituted dimethyldiphenylsilanes 2a–e

Representative example 4-(dimethylphenylsilyl)bromobenzene (2e). Chlorodimethylphenylsilane (2.00 g, 11.7 mmol) was added to a solution of 4-bromophenyllithium (11.7 mmol) in 20 ml of diethyl ether. The white suspension was stirred overnight and 15 ml of water was then added. The organic layer was separated, washed with 15 ml of water dried over magnesium sulphate, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica (with chloroform as eluent) and then recrystallized from diethyl ether. Yield 2.79 g (9.6 mmol, 82%) of a white solid, m.p. 21°C . ^1H NMR (ppm): δ 7.51 (m, 4H, Ar-H); 7.37 (m, 5H, Ar-H); 0.55 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 137.6; 137.2; 135.8; 134.1; 131.0; 129.2; 127.9; 124.0; -2.5 (SiMe). IR (KBr, cm^{-1}): ν 1250, 830–800 (Si-Me); 1110 (Si-Ar).

4-(Dimethylphenylsilyl)-N,N-dimethylaniline (2a). This compound was purified by distillation (b.p. $180\text{--}183^\circ\text{C}$, 0.01 mmHg). Yield 2.22 g (8.69 mmol, 30%) of a colourless oil. ^1H NMR (ppm): δ 7.56 (m, 2H, Ar-H); 7.43, 6.76 (AA'XX', $2 \times 2\text{H}$, Ar-H); 7.36 (m, 3H, Ar-H); 2.99 (s, 6H, NMe); 0.54 (s, 6H, SiMe). ^{13}C NMR (ppm) δ 151.3; 139.4; 135.3; 123.1; 134.2; 128.8; 127.7; 112.0; 40.2 (NMe); -2.0 (SiMe). IR (NaCl, cm^{-1}): ν 2790 (NMe₂); 1250, 850–800 (Si-Me); 1110 (Si-Ar).

4-(Dimethylphenylsilyl)anisole (2b). Compound **2b** was crystallized from methanol at -20°C (at room temperature it is a colourless liquid). Yield 3.71 g (15.3 mmol, 56%). ^1H NMR (ppm): δ 7.53 (m, 2H, Ar-H); 7.47,

6.93 (AA'XX', $2 \times 2\text{H}$, Ar-H); 7.36 (m, 3H, Ar-H); 3.82 (s, 6H, NMe); 0.55 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 160.5; 138.8; 135.7; 133.1; 129.1; 128.9; 127.8; 113.6; 55.0 (OMe); -2.0 (SiMe). IR (NaCl, cm^{-1}): ν 2820, 1270, 1030 (OMe); 1250, 850–800 (Si-Me); 1110 (Si-Ar).

4-(Dimethylphenylsilyl)thioanisole (2c). Recrystallization from hexane gave a white solid. Yield 1.37 g (5.1 mmol, 62%), m.p. 57°C . ^1H NMR (ppm): δ 7.51 (m, 2H, Ar-H); 7.43, 7.24 (AA'BB', $2 \times 2\text{H}$, Ar-H); 7.36 (m, 3H, Ar-H); 2.48 (s, 3H, SMe); 0.54 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 139.9; 138.2; 134.6; 134.1; 129.1; 127.8; 127.0; 125.6; 15.3 (SMe); -2.4 (SiMe). IR (KBr, cm^{-1}): ν 1320 (SMe); 1245, 850–800 (Si-Me); 1120 (Si-Ar).

Di(4-substituted phenyl)dimethylsilanes 3a–e

Representative examples di(4-bromophenyl)dimethylsilane (3e). A solution of dichlorodimethylsilane (3.85 ml, 32 mmol) in 35 ml of diethyl ether was added dropwise to a solution of 4-bromophenyllithium (63.6 mmol) in 150 ml of diethyl ether. The mixture was stirred for 5 h at room temperature, then 30 ml water were added. The organic layer was separated, washed twice with 25 ml of water, dried over magnesium sulphate, filtered and concentrated under reduced pressure. Recrystallization of the solid product from methanol gave 8.33 g (22.5 mmol, 70%) of white crystals, m.p. 72°C . ^1H NMR (ppm): δ 7.52, 7.37 (AA'BB', $2 \times 4\text{H}$, Ar-H); 0.54 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 136.4; 135.7; 131.1; 124.2; -2.6 (SiMe). IR (KBr, cm^{-1}): ν 1250, 830 (Si-Me); 1105 (Si-Ar).

Dimethyldi(4-(N,N-dimethylamino)phenyl)silane (3a). Yield 4.31 g (29.2 mmol, 86%), m.p. 77°C . MS: m/z 298 (M^+); 283 ($\text{M} - \text{Me}$)⁺. ^1H NMR (ppm): δ 7.41, 6.73 (AA'XX', $2 \times 4\text{H}$, Ar-H); 2.97 (s, 12H, NMe); 0.46 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 150.9; 135.3; 124.2; 112.0; 40.3 (NMe); -1.8 (SiMe). IR (KBr, cm^{-1}): ν 2790 (NMe₂); 1250, 850–800 (Si-Me); 1110 (Si-Ar).

Di(4-methoxyphenyl)dimethylsilane (3b). Two recrystallizations from hexane gave a white crystalline solid. Yield 3.50 g (25.2 mmol, 70%), m.p. 49°C . MS: m/z 272 (M^+); 257 ($\text{M} - \text{Me}$)⁺. ^1H NMR (ppm): δ 7.45, 6.92 (AA'XX', $2 \times 4\text{H}$, Ar-H); 3.82 (s, 6H, OMe); 0.51 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 160.4; 135.6; 129.5; 113.6; 55.0 (OMe); -2.0 (SiMe). IR (KBr, cm^{-1}): ν 2820, 1270, 1030 (OMe); 1250, 850–800 (Si-Me); 1105 (Si-Ar).

Dimethyldi(4-(methylthio)phenyl)silane (3c). was recrystallized from hexane. Yield 11.68 g (76.8 mmol,

78%), m.p. 57°C. ^1H NMR (ppm): δ 7.42, 7.24 (AA'BB', $2 \times 4\text{H}$, Ar-H); 2.48 (s, 6H, SiMe); 0.53 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 140.0; 134.5; 134.1; 125.6; 15.3 (SiMe); -2.4 (SiMe). IR (KBr, cm^{-1}): ν 1320 (SiMe); 1255, 830–800 (Si–Me); 1120 (Si–Ar).

Diphenyldimethylsilane (2d = 3d). ^1H NMR (ppm): δ 7.60 (m, 4H, Ar-H); 7.44 (m, 6H, Ar-H); 0.64 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 138.6; 134.6; 129.6; 128.3; -1.9 (SiMe). IR (NaCl, cm^{-1}): ν 1250, 830–800 (Si–Me); 1110 (Si–Ar).

Conversion of bromides into aldehydes

Representative example di(4-formylphenyl)dimethylsilane (3f). *n*-Butyllithium (28.3 mmol) in hexane was added to an ice-cooled solution of **3e** (5.10 g, 13.8 mmol) in 60 ml of diethyl ether. The stirred mixture was gradually warmed to room temperature and after 4.5 h it was cooled in an ice-bath and subsequently DMF (10 ml, 129 mmol) was added. After stirring for 17 h, the white suspension was added to 50 ml of water. The layers were separated and the water layer was extracted twice with 25 ml of diethyl ether. The combined extracts were dried over sodium sulphate, filtered and evaporated under reduced pressure. Recrystallization from hexane afforded 2.86 g (10.6 mmol, 77%) of a white solid, m.p. 71°C. ^1H NMR (ppm): δ 10.03 (s, 2H, CHO); 7.86, 7.68 (AA'BB', $2 \times 4\text{H}$, Ar-H); 0.64 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 192.4 (CHO); 145.6; 136.9; 134.7; 128.8; -2.8 (SiMe). IR (KBr, cm^{-1}): ν 1705 (C=O); 1250, 850–800 (SiMe); 1105 (Si–Ar).

4-(Trimethylsilyl)benzaldehyde (1f). This compound was obtained as a light-yellow liquid after column chromatography with chloroform as eluent. Yield 2.08 g (11.6 mmol, 59%). ^1H NMR (ppm): δ 10.02 (s, 1H, CHO); 7.84, 7.69 (AA'BB', $2 \times 2\text{H}$, Ar-H); 0.31 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 192.6 (CHO); 149.2; 136.5; 133.8; 128.6; -1.4 (SiMe). IR (NaCl, cm^{-1}): ν 1705 (C=O); 1250, 850–800 (SiMe); 1100 (Si–Ar).

4-(Dimethylphenylsilyl)benzaldehyde (2f). Purification by column chromatography with chloroform as eluent gave a colourless liquid. Yield 0.96 g (4.02 mmol, 78%). ^1H NMR (ppm): δ 10.00 (s, 1H, CHO); 7.84, 7.69 (AA'BB', $2 \times 2\text{H}$, Ar-H); 7.52 (m, 2H, Ar-H); 7.38 (m, 3H, Ar-H); 0.60 (s, 6H, SiMe). IR (NaCl, cm^{-1}): ν 1705 (C=O); 1250, 850–800 (SiMe); 1105 (Si–Ar).

Conversion of bromides into cyanides

Representative example 4-(dimethylphenylsilyl)cyanobenzene (2g). A mixture of 4-(dimethylphenylsilyl)

bromobenzene (**2e**, 1.03 g, 3.5 mmol) and copper(I) cyanide (0.39 g, 4.4 mmol) in 5 ml of DMF was boiled for 5 h, then allowed to cool to room temperature and added to 75 ml of concentrated ammonia solution. The mixture was stirred vigorously as air was passed through the suspension for 4 h. After extraction with chloroform (3×20 ml), the extract was concentrated to 10 ml and 50 ml of hexane were added. The solution was washed three times with 50 ml of water, dried over magnesium sulphate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (eluent chloroform–hexane (1:1, v/v)) to give 0.76 g (3.20 mmol, 91%) of a colourless liquid. ^1H NMR (ppm): δ 7.63, 7.59 (AA'BB', $2 \times 2\text{H}$, Ar-H); 7.53 (m, 2H, Ar-H); 7.38 (m, 3H, Ar-H); 0.60 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 145.4; 136.5; 134.7; 134.1; 131.1; 129.7; 128.2; 119.0 (CN); 112.8; -2.7 (SiMe). IR (NaCl, cm^{-1}): ν 2240 (CN); 1250, 840–800 (Si–Me); 1115 (Si–Ar).

4-(Trimethylsilyl)cyanobenzene (1g). This compound was purified by distillation (b.p. 46–47°C, 0.05 mmHg) followed by column chromatography (chloroform–hexane (1:1, v/v)). Yield 1.01 g (15.2 mmol, 58%) of a colourless liquid. ^1H NMR (ppm): δ 7.57, 7.51 (AA'BB', $2 \times 2\text{H}$, Ar-H); 0.29 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 147.2; 133.8; 130.8; 118.8 (CN); 112.4; -1.5 (SiMe). IR (NaCl, cm^{-1}): ν 2240 (CN); 1255, 850–800 (Si–Me); 1105 (Si–Ar).

Di(4-cyanophenyl)dimethylsilane (3g). Compound **3g** was obtained as white crystals after crystallization from methanol. Yield 1.77 g (6.74 mmol, 50%), m.p. 100°C. ^1H NMR (ppm): δ 7.63, 7.58 (AA'BB', $2 \times 4\text{H}$, Ar-H); 0.61 (s, 6H, SiMe). ^{13}C NMR (ppm): δ 143.5; 134.5; 131.3; 118.7 (CN); 113.3; -3.1 (SiMe). IR (KBr, cm^{-1}): ν 2235 (CN); 1260, 850–800 (Si–Me); 1100 (Si–Ar).

(2,2-Dicyanoethenyl)-4-(trimethylsilyl)benzene (1h). A solution of 4-(trimethylsilyl)benzaldehyde (**1f**, 2.08 g, 11.7 mmol), malodinitrile (0.78 g, 11.8 mmol) and one drop of piperidine in 20 ml of methanol was stirred for 2 h. The solid that formed was filtered off and the filtrate was evaporated until further solid separated, and the latter was filtered off. The combined solids were recrystallized from hexane to give 0.56 g (2.5 mmol, 21%) of a light-yellow solid, m.p. 88°C. MS: m/z 226 (M^+); 211 ($\text{M} - \text{Me}$) $^+$. ^1H NMR (ppm): δ 7.85, 7.69 (AA'BB', $2 \times 2\text{H}$, Ar-H); 7.76 (s, 1H, $\text{CH}=\text{C}(\text{CN})_2$); 0.31 (s, 9H, SiMe). ^{13}C NMR (ppm): δ 160.1 ($\text{CH}=\text{C}(\text{CN})_2$); 150.3; 134.4; 131.0; 129.4; 113.8, 112.6 (CN); 82.8 ($\text{CH}=\text{C}(\text{CN})_2$); -1.5 (SiMe). IR (KBr, cm^{-1}): ν 2230 (CN); 1660 (C=C); 1250, 850–800 (Si–Me); 1120 (Si–Ar).

Preparation of dicyanoethenyl compounds in benzene

Representative example di(4-(2,2-dicyanoethenyl)phenyl)dimethylsilane (3h). In contrast to **1h**, compound **3h** could only be obtained in a reasonable yield by removing the water by azeotropic distillation with benzene. A mixture of di(4-formylphenyl)dimethylsilane (**3f**, 0.86 g, 3.2 mmol), malodinitrile (0.43 g, 6.5 mmol) and two drops of piperidine in 40 ml of benzene was boiled for 20 h in a flask equipped with a Dean–Stark water separator. The brown solution was then concentrated under reduced pressure. Flash column chromatography with chloroform as eluent, followed by recrystallization from diethyl ether–hexane (10:1, v/v) gave 0.46 g (1.3 mmol, 39%) of a light-yellow solid, m.p. 94°C. ¹H NMR (ppm): δ 7.87, 7.67 (AA'BB', 2 × 4H, Ar–H); 7.78 (s, 2H, CH=C(CN)₂); 0.64 (s, 6H, SiMe). ¹³C NMR (ppm): δ 159.6 (CH=C(CN)₂); 146.0; 135.1; 131.7; 129.6; 113.6, 112.4 (CN); 83.7 (CH=C(CN)₂); –3.1 (SiMe). IR (KBr, cm^{–1}): ν 2220 (CN); 1255, 830–800 (Si–Me); 1100 (Si–Ar).

[4-(2,2-Dicyanoethenyl)phenyl]dimethylphenylsilane (2h). This compound was prepared by the procedure described for **3h**. It was obtained as a light-yellow solid in 27% yield (0.31 g, 1.1 mmol) after flash column chromatography with chloroform as eluent and recrystallization from pentane; m.p. 77°C. ¹H NMR (ppm): δ 7.84, 7.68 (AA'BB', 2 × 2H, Ar–H); 7.76 (s, 1H, CH=C(CN)₂); 7.50 (m, 2H, Ar–H); 7.40 (m, 3H, Ar–H); 0.60 (s, 6H, SiMe). ¹³C NMR (ppm): δ 160.0 (CH=C(CN)₂); 148.3; 136.4; 135.2; 134.1; 131.2; 129.7; 129.5; 128.1; 113.8 (CN); 112.6 (CN); 83.0 (CH=C(CN)₂); –2.8 (SiMe). IR (KBr, cm^{–1}): ν 2220 (CN); 1660 (C=C); 1250, 830–800 (Si–Me); 1100 (Si–Ar).

[4-(Methylsulphonyl)phenyl]trimethylsilane (1i). To a solution of potassium permanganate (7.03 g, 44.5 mmol) in 110 ml of 0.9% sodium hydroxide solution was added. 4-(trimethylsilyl)thioanisole (**1c**, 4.00 g, 20.4 mmol). The mixture was refluxed for 24 hours [21] and then extracted with 200 ml followed by 2 × 15 ml of chloroform. After evaporation of the chloroform, the residual solid was recrystallized from hexane. Yield 3.51 g (15.4 mmol, 75%) of white crystals, m.p. 83°C. ¹H NMR (ppm): δ 7.90, 7.71 (AA'BB', 2 × 2H, Ar–H); 3.04 (s, 3H, SO₂Me); 0.30 (s, 9H, SiMe). ¹³C NMR (ppm): δ 148.4; 140.7; 134.2; 126.1; 44.5 (SO₂Me); –1.4 (SiMe). IR (KBr, cm^{–1}): ν 1310, 1145 (SO₂); 1250, 850–800 (Si–Me); 1100 (Si–Ar).

Dimethyl[4-(methylsulfonyl)phenyl]phenylsilane (2i). A solution of 0.4 ml (4.6 mmol) of 35% aqueous hydrogen peroxide in 5 ml of glacial acetic acid was added to a cooled (ice-bath) solution of **2c** (0.50 g, 1.94 mmol) in

10 ml of acetic acid [22]. The mixture was stirred for 16 h at room temperature and the temperature was then increased in 15°C steps to the reflux temperature, the mixture being stirred for 2 h after each temperature increase. After a total of 64 h of refluxing the volatiles were removed under reduced pressure and the crude residue was subjected to flash chromatography with acetone as eluent. Column chromatography with chloroform as eluent followed by recrystallization from diethyl ether–pentane (10:1 v/v) gave white crystals. Yield 0.39 g (1.34 mmol, 69%), m.p. 52°C. ¹H NMR (ppm): δ 7.89, 7.71 (AA'BB', 2 × 2H, Ar–H); 7.50 (m, 2H, Ar–H); 7.40 (m, 3H, Ar–H); 3.04 (s, 3H, SO₂Me); 0.60 (s, 6H, SiMe). ¹³C NMR (ppm): δ 146.4; 140.9; 136.5; 135.0; 134.1; 129.7; 128.1; 126.2; 44.5 (SO₂Me); –2.7 (SiMe). IR (KBr, cm^{–1}): ν 1310, 1150 (SO₂), 1250, 850–800 (Si–Me); 1115 (Si–Ar).

Dimethyldi[4-(methylsulphonyl)phenyl]silane (3i). This compound was prepared by the procedure described for **2i**, but 20 days were required for completion of the reaction and during this period three additional aliquots of hydrogen peroxide (in total 20% of the starting amount) were added. The product was purified by flash chromatography with acetone as eluent followed by recrystallization from ethanol to give a white crystalline solid in 66% yield (2.01 g, 5.4 mmol), m.p. 181°C. ¹H NMR (ppm): δ 7.91, 7.68 (AA'BB', 2 × 4H, Ar–H); 3.04 (s, 6H, SO₂Me); 0.63 (s, 6H, SiMe). ¹³C NMR (ppm): δ 144.5; 141.6; 135.0; 126.5; 44.4 (SO₂Me); –2.9 (SiMe). IR (KBr, cm^{–1}): ν 1310, 1150 (SO₂); 1250, 850–800 (Si–Me); 1100 (Si–Ar).

3. Results and discussion

3.1. Synthesis

4-Substituted trimethylsilylbenzenes **1a–e** were prepared by reaction of the corresponding phenyllithium compounds with chlorotrimethylsilane (Scheme 1, reaction (1)). The lithium derivatives were usually obtained by treatment of 4-substituted phenyl bromides with *n*-butyllithium but, in the case of the dimethylamino and methoxy substituents, lithium was used [23]. Compounds **2a–e** and **3a–e** were prepared analogously by reaction of the phenyllithium compounds with either chlorotrimethylphenylsilane or 0.5 equiv. of dichlorodimethylsilane. Bromides **1e–3e** were converted into aldehydes **1f–3f** by treatment with *n*-butyllithium and DMF, and Knoevenagel condensation of the aldehydes with malodinitrile afforded the dicyanoethylenes **1h–3h** (reaction (5)). The cyanides **1g–3g** were obtained from the bromides **1e–3e** by treatment with copper(I) cyanide in DMF [24,25]. Oxidation of the thioanisoles **1c–3c**

Table 1

Chemical shifts (δ in ppm) and PM3-calculated total atomic charges (q) of selected atoms of compounds **1–3a–i**

Compound	δ Si	q Si	δ C1	q C1	δ CH ₃	q CH ₃	δ C1'	q C1'	δ C4'	q C4'
1a	−5.30	0.473	125.7	−0.262	−0.73	−0.256				
1b	−4.62	0.477	134.8	−0.270	−0.84	−0.256				
1c	−4.11		136.4		−1.15					
1d	−4.10	0.478	140.5	−0.234	−1.11	−0.257				
1e	−3.45	0.485	139.2	−0.231	−1.18	−0.259				
1f			149.2		−1.37					
1g	−2.53	0.491	147.2	−0.218	−1.53	−0.260				
1h	−2.61	0.489	150.3	−0.215	−1.48	−0.260				
1i	−2.58		148.4		−1.41					
2a	−8.92	0.515	123.1	−0.252	−2.02	−0.242	139.4	−0.220	128.8	−0.095
2b	−8.46	0.519	133.1	−0.256	−2.04	−0.242	138.8	−0.221	129.1	−0.095
2c	−8.07		138.2		−2.38		138.2		129.1	
2d	−8.04	0.518	138.6	−0.223	−1.89	−0.243	138.6	−0.223	129.6	−0.095
2e	−7.54	0.525	137.2	−0.221	−2.45	−0.243	137.2	−0.228	127.9	−0.093
2g	−6.97	0.531	145.4	−0.207	−2.65	−0.244	136.5	−0.231	129.7	−0.091
2h	−7.10	0.528	148.3	−0.209	−2.76	−0.244	136.4	−0.232	129.7	−0.091
2i	−7.04		146.4		−2.66		136.5		129.7	
3a	−9.77	0.511	124.3	−0.248	−1.78	−0.240				
3b	−8.84	0.516	135.6	−0.257	−1.98	−0.241				
3c	−8.10		134.1		−2.36					
3d	−8.04	0.518	138.6	−0.223	−1.89	−0.243				
3e	−7.01	0.530	136.4	−0.224	−2.56	−0.245				
3f			145.6		−2.82					
3g	−5.95	0.542	143.5	−0.214	−3.05	−0.246				
3h	−6.22	0.541	146.0	−0.211	−3.08	−0.246				
3i	−6.05		144.5		−2.90					

For numbering of the atoms, see Scheme 1. Substituents: **a** NMe₂ ($\sigma_p = -0.63$), **b** OMe (-0.28), **c** SMe (0.05), **d** H (0), **e** Br (0.26), **f** CHO (0.45), **g** C≡N (0.70), **h** CH=C(CN)₂ (0.70), **i** SO₂Me (0.73) [31].

with either potassium permanganate [21] or hydrogen peroxide [22] gave the sulphones **1i–3i**¹.

3.2. ²⁹Si and ¹³C NMR spectroscopy

It is well documented that ¹³C and ²⁹Si chemical shifts are in general dominated by the paramagnetic

shielding term σ^{para} [26], which can be approximated by

$$\sigma^{\text{para}} \approx -C \frac{Q + \Sigma p}{r^3}$$

on the assumption that Si d orbitals do not contribute [27,28]; Q denotes the electron density on the nucleus, Σp the sum of bond orders, r the nucleus–electron distance and C is a constant. Thus, for closely related compounds, chemical shifts are mainly determined by the nuclear charge and the electron–nucleus distance. Indeed, in numerous cases linear correlations have been

¹ With potassium permanganate, the thionanisoles were oxidized partly to the sulphonic acids. This was avoided by using hydrogen peroxide.

Table 2

Linear regression analysis of the ²⁹Si and ¹³C chemical shifts of atoms Si, C4, CH₃, C1' and C4' versus Hammett substituent constants ($\delta = \rho\sigma_p + b$) and calculated total atomic charges ($\delta = \rho q + b$) of compounds **1–3**, with correlation coefficients r

Compound type	Atom	σ_p			q		
		ρ	b	r	ρ	b	r
1	Si	2.07 ± 0.06	−4.06 ± 0.03	0.997	147 ± 12	−74.8 ± 5.6	0.988
2	Si	1.43 ± 0.06	−8.04 ± 0.03	0.995	118 ± 14	−69.5 ± 7.5	0.972
3	Si	2.80 ± 0.13	−8.03 ± 0.06	0.994	112 ± 13	−66.5 ± 6.9	0.974
1	C1	16.8 ± 1.9	137.2 ± 1.0	0.962	346 ± 104	222 ± 25	0.888
2	C1	16.2 ± 1.7	135.3 ± 0.9	0.974	379 ± 118	224 ± 27	0.880
3	C1	14.0 ± 2.2	135.3 ± 1.2	0.932	315 ± 150	210 ± 35	0.773
1	CH ₃	−0.58 ± 0.04	−1.07 ± 0.02	0.983	207 ± 19	52.3 ± 5.0	0.987
2	CH ₃	−0.54 ± 0.06	−2.30 ± 0.03	0.975	313 ± 39	73.6 ± 9.5	0.978
3	CH ₃	−0.96 ± 0.06	−2.33 ± 0.03	0.988	188 ± 18	43.2 ± 4.5	0.986
2	C1'	−2.27 ± 0.14	138.1 ± 0.1	0.990	194.1 ± 3.9	250 ± 17	0.993
2	C4'	0.62 ± 0.47	129.0 ± 0.3	0.510	171 ± 213	145 ± 20	0.420

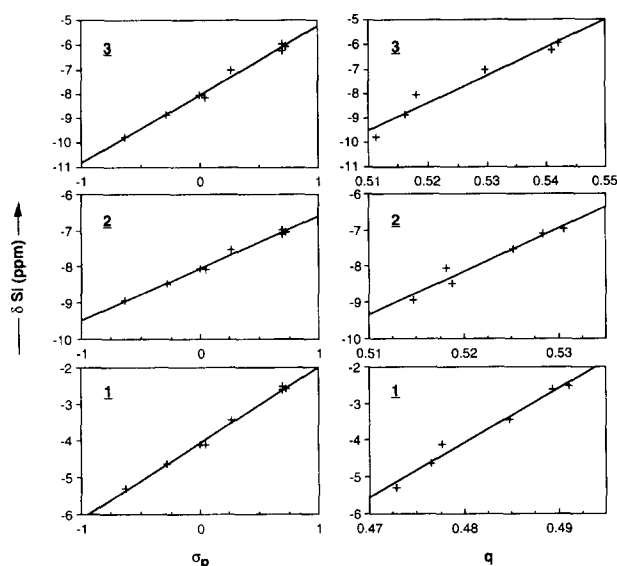


Fig. 1. ^{29}Si NMR chemical shifts plotted vs. Hammett's σ_p constants (left) and PM3-calculated total atomic charges (right).

found between ^{13}C and ^{29}Si chemical shifts and calculated electron densities or Hammett substituent constants [26,28,29].

Within the series 1–3, the signals from the silicon atoms and carbon atoms of the Si-Me groups and those numbered C1, C1' and C4' (C4' only in 2a–e) were used to examine the possible transmission of electronic effects. The chemical shifts and PM3-calculated total atomic charges are listed in Table 1. The assignments of the ^{13}C NMR spectra were based on additivity rules [26], data for related compounds and available literature data [30]. The chemical shifts exhibit linear relationships with both the Hammett σ_p constants [31] and the PM3-calculated total atomic charges, as is shown in Fig. 1 for the ^{29}Si shifts. The parameters for these relationships are given in Table 2. It should be noted that the ^{13}C NMR data for the unsubstituted compounds 1d, 2d and 3d were omitted since they deviate from the observed linear relationships. In respect of the positions C1 and C1' this can be justified by pointing to the fact that the chemical shifts for the unsubstituted compounds are wholly determined by the silicon substituent, and *ipso* carbons are known not to show a linear correlation with substituent constants [26].

The linear relationship found between the ^{29}Si chemical shifts and the Hammett substituent constants in the range spanning both electron donors and acceptors for the series 1 is in line with earlier investigations on the substituent behaviour of the trimethylsilyl group. This group acts as an inductive donor and a mesomeric acceptor [32–35]. As is indicated by its Hammett substituent constants σ_i (inductive, -0.10) and σ_R^0 (mesomeric, 0.06) [31], the two effects tend to be equally strong [34]. The electron-donating or -accepting effect of the trimethylsilyl group attached to an aromatic

nucleus is therefore determined by the nature of any additional substituent [36]. If the latter is an electron donor, the trimethylsilyl group acts as an electron acceptor; if it is an acceptor, the trimethylsilyl group acts as a donor. This is in accordance with the observation that there is no bending at $\sigma_p = 0$ in the line for series 1. The dimethylphenylsilyl group is, according to its Hammett constants ($\sigma_i = 0.02$, $\sigma_R^0 = 0.05$ [31]), a weak inductive and mesomeric acceptor. Its behaviour in the presence of additional substituents appears, however, to be comparable to that of the trimethylsilyl group, since straight lines without bending at $\sigma_p = 0$ were obtained for the series 2 and 3.

The slope ρ in the regression analysis for the ^{29}Si NMR data for compounds 2a–i is significantly smaller than that for 1a–i. This represents compelling evidence for the delocalization of the induced charge over the second phenyl group, implying that the silicon spacer is able to transmit electronic effects in the ground state. The value of ρ for the doubly substituted diphenylsilanes 3 is close to twice the value found for the monosubstituted silanes 2, that is, the effects of the two substituents are additive, no additional interaction being observed with respect to that for the monosubstituted compounds.

As shown by the data in Table 2, the linearities of the plots for the ^{13}C NMR shifts are less satisfactory than those for the ^{29}Si shifts. It is noteworthy that the ^{13}C chemical shifts for the methyl groups of compounds 1–3a–i and C1' of 2a–i decrease with increasing electron-withdrawing power of the substituents, i.e. an upfield shift is observed. Usually an increase in the electron-withdrawing power of substituents lowers the electron density on an atom, leading to lower shielding and hence a downfield chemical shift. Schaeffer et al. [37] observed this inverse substituent effect for phenyltrimethylsilane derivatives. They pointed out that both inductive and resonance effects contribute, but offered no further explanation. It can, however, be attributed to bond polarization effects [38–40]. Owing to electronegativity differences, carbon atoms directly bonded to silicon possess a partial negative charge. As shown above by the ^{29}Si NMR data, introduction of an electron-withdrawing substituent renders the silicon atom more positive, and the silicon–carbon bonds become more polarized. The smaller electron density on the carbon atoms shifts their signals to lower field. It is noteworthy that a similar upfield shift for Si–Me ^{13}C resonances is found in 1-pyrenyl-substituted oligosilylene chains in the presence of an α -trimethylsilyl group [41]. The authors attributed this shift to electron donation by the trimethylsilyl group. Our results suggest that the influence of substituents on the Si–Me ^{13}C NMR shifts is more complex.

From the linear dependence of the chemical shift for atom C1' in compounds 2a–i on the Hammett constants,

it is evident that the unsubstituted phenyl group is affected by substitution at position 4 of the other phenyl group. The effect is small, but larger than that at the methyl groups. At carbon atoms C4' in **2a–i** the influence of the substituent X is no longer detectable and there is a scattering of the points. In the light of the knowledge that inductive effects are negligible at *para* positions and that the effect on the C1' atom is already weak, this does not come as a surprise.

The lines for the carbon atoms C1 are essentially identical, with comparable slopes and intercepts. Consequently, the shifts of the C1 atoms seem to be unaffected by the groups on the other side of the silicon atoms, and electronic interactions through silicon cannot be inferred from the data. It should be kept in mind, however, that such an interaction may exist (especially in the series **3**) but be insignificant compared with the influence of the substituent directly bound to the ring containing C1.

The conclusions are corroborated by examination of the PM3-calculated total atomic charges. Linear correlations are observed between the relevant chemical shifts and charges (Table 2). Although the charges on silicon seem to be overestimated, the change in the ^{29}Si NMR shift with the electronic properties of the substituent X is satisfactorily reflected. Although the correlation between the chemical shifts of atoms C1 and the calculated charges is poor, the same applies for the ^{13}C chemical shifts. This establishes that the inverse substituent effect must be attributed to bond polarization effects. With respect to the behaviour of C4' in **2a–i**, the PM3 calculations reveal a rough trend of decreasing negative charge with increasing σ_p constant. It may well be that the charges on the C4' atoms are so small that other factors influencing the chemical shift dominate.

Both the spectroscopic and theoretical data imply that the SiMe_2 spacer transmits substituent effects in the ground state. It is thus of interest to assess the extent to which the presence of the silicon atom affects the results and so we compared our data with those available for related 4-substituted (**4** [42]) and 4,4'-disubstituted diphenylmethanes (**5** [43]), which we reanalysed using our approach (Table 3). The conclusions are in accordance with those reported in the papers from which the data were taken. In the series **4** good linear relationships are found for atoms C1 and C1' and the substituent constants σ_p . In keeping with the results for **2a–i**, the C1' atom exhibits the inverse substituent effect, but with a considerably smaller slope ($\rho = -1.76$ in **4** and -2.27 in **2a–i**). Furthermore, the linear relationship for the CH_2 spacer ($r = 0.837$) is less satisfactory than that for the SiMe_2 spacer ($r = 0.995$). It is, however, noteworthy that a relatively good relationship with positive ρ value is observed for atoms C4' in **4**. Nevertheless, it can be concluded that the SiMe_2 spacer

Table 3

Linear regression analysis of ^{13}C chemical shifts of selected atoms of 4-substituted (**4**) and 4,4'-disubstituted diphenylmethanes (**5**) versus Hammett substituent constants σ_p ($\delta = \rho\sigma_p + b$), with correlation coefficients r

Compound	Atom	ρ	b	r
4	CH_2	0.47 ± 0.11	41.61 ± 0.04	0.837
4	C1	14.1 ± 1.2	139.0 ± 0.5	0.970
4	C1'	-1.76 ± 0.2	141.72 ± 0.08	0.953
4	C4'	0.78 ± 0.17	126.48 ± 0.07	0.847
5	CH_2	0.6 ± 0.3	41.0 ± 0.1	0.499
5	C1	12.5 ± 1.4	138.1 ± 0.5	0.951

^{13}C NMR chemical shifts were taken from the literature [42,43].

is a better transmitter of electronic effects and displays a better interaction with 4-substituents than the CH_2 spacer. This conclusion is further supported by the analysis of the data for the 4,4'-disubstituted diphenylmethanes (**5**) [43]. There is no convincing linear relationship between the ^{13}C NMR shift by the CH_2 group ($r = 0.499$) and substituent constants σ_p , whereas for the compounds of series **3a–i** the linearity is good ($r = 0.994$). At the C1 atoms in compounds **5** the quality of the relationship is still comparable to that found in their silicon analogues **3a–i**.

In summary, the SiMe_2 spacer is a better transmitter of substituent effects of electronic effects than a CH_2 spacer. For the SiMe_2 spacer the transmission occurs via a bond polarization mechanism. Through-space overlap between p orbitals on atoms C1 and C1' [44] is unlikely to provide an explanation for the described effects, since they are also observed at the methyl groups of the SiMe_2 spacer.

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