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Carbon–silicon hyperconjugation X-ray structural study of *N*-methyl-4-trimethylsilylmethylpyridinium triflate

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Abstract

Hyperconjugation between the CH_2–Si bond and the charged pyridinium π system in the *N*-methyl 4-trimethylsilylmethyl pyridinium ion (**8**), manifests in the crystal structure as lengthening of the CH_2–Si bond, shortening of the CH_2–C_{ipso} bond and smaller but systematic effects on the C–C bond distances within the pyridinium ring. The structural effects are supported in solution by systematic effects on the ^{29}Si–^{13}C and ^{13}C–^{13}C one-bond coupling constants. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hyperconjugation; X-ray; π-Systems

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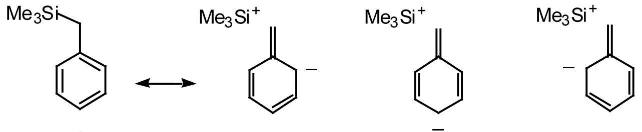
1. Introduction

The C–Si bond interacts by strong hyperconjugation with adjacent π systems of an aromatic ring in the neutral ground state [1–3]. This has been referred to as sacrificial or isovalent hyperconjugation [4] and can be represented by the valance structures **1**–**4**.



1 **2** **3** **4**

The effects of this hyperconjugation on the properties of the aromatic ring have been investigated in solution by ^{19}F- [5–9], ^{13}C- [6,10,11], and ^{1}H-NMR, infrared [12–16], and by electron spectroscopic studies of the charge transfer complexes of various benzyl Group 4 derivatives with π-deficient species [1,17–21]. Further spectroscopic evidence for the effects of C–M (M = Si, Ge, Sn) hyperconjugation was provided from the one-bond ^{13}C–M (M = ^{29}Si, ^{119}Sn) and ^{13}C–^{13}C coupling constants in the series of 4-substituted benzyl-silanes, -germanes, and -stannanes **5**–**7** [22]. Although the effects of σ–π conjugation between C–Si bonds and neighbouring π systems is well characterised in solution, to the best of our knowledge there is no structural evidence. As part of our on-going interest in the structural properties of Group 4 metal substituted organic compounds [23–28], we were interested to see whether the effects of σ–π conjugation in trimethylsilylmethyl substituted aromatic systems would lead to observable structural effects. The structural effects anticipated were lengthening of the Si–CH_2 distance, and shortening of the CH_2–C_{ipso} distance, reflecting contributions of the resonance forms **1**–**4** to the ground state structure. We chose as our system for study the *N*-methyl trimethylsilylmethylpyridinium ion (**8**), this system was chosen for two reasons; firstly the high electron demand of the charged pyridinium ring should ensure strong hyperconjugation with the C–Si bond, and secondly, crystals suitable for an accurate X-ray structural study should be available by appropriate choice of counterion.

The precursor to **8**, trimethylsilylmethylpyridine (**9**) was prepared according to Scheme 1.

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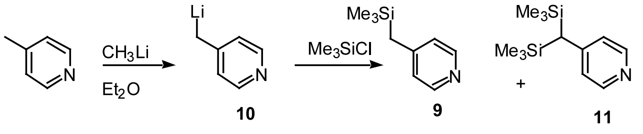
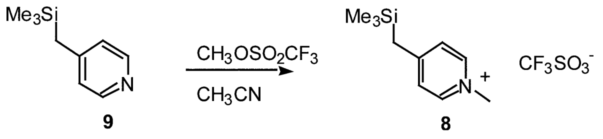


Scheme 1.

4-Picoline was treated with methyl lithium in ether giving the intermediate lithio species **10** as a precipitate, treatment of this mixture with trimethylsilyl chloride gave a mixture of 4-trimethylsilylmethylpyridine (**9**) (60%) as well as the bis-silylated pyridine **11** (20%) and picoline starting material. It was found that the bis-silylated derivative **11** could be avoided by inverse addition of a slurry of **10** in ether to a solution of trimethylsilyl chloride in ether. Using the latter method the trimethylsilyl-substituted picoline **9** was obtained in quantitative yield. Methylation of **9** was carried out using either methyl iodide or methyl triflate (Scheme 2).

The triflate derivative of **8** gave excellent crystals for an accurate X-ray structural analysis, however these were of low solubility, therefore the more soluble iodide salt was employed for characterisation purposes. For comparison purposes the methylpicolinium salt **12** was also prepared, it was found that the tosylate derivative of **12** gave crystal most suitable for X-ray analysis.

The X-ray crystal structures of triflate **8** and tosylate **12** were determined at 130 K to minimise the unwanted effects of thermal motion. Details of the data collection and refinement for compounds **8** and **12** are presented in Table 1, selected bond distances, angles and dihedral angles are presented in Table 2, and thermal ellipsoid plots are presented in Figs. 1 and 2, respectively. The triflate **8** lies on a crystallographic plane of symmetry with the silicon, methylene, *ipso* carbon, nitrogen and methyl carbon lying on the mirror plane. The Si–CH$_2$–C$_{ipso}$–C dihedral angle is 88.8(2)° to both *ortho* positions, a conformation which is favoured on steric grounds and also on electronic grounds as it allows for effective overlap between the CH$_2$–Si bond and the pyridinium π system, the slight deformation of the pyridine ring from planarity which is suggested by this dihedral angle possibly reflects contributions of the resonance structure **8′** (below) to the ground state structure. Comparison of the C–C bond distances (Table 2) between the two structures also provides evidence for the presence of significant σ–π conjugation between the Si–CH$_2$ σ bonding orbital and the aromatic π system in **8**. For example the CH$_2$–C$_{ipso}$ distance in **8** is 1.486(3) Å, this is significantly shorter than the CH$_3$–C$_{ipso}$ distance in **12** which is 1.502(3) Å, there are smaller, barely significant effects apparent within the pyridine ring of **8** thus the C$_i$–C$_o$ and C$_o$–C$_m$ distances are 1.398(2) and 1.367(2) Å, respectively. The corresponding distances in **12** are 1.388(3) and 1.372(3). The Si–CH$_2$distance is 1.895(3) Å, which is significantly longer than the average values of 1.878 Å which we obtained from a survey of the Cambridge Crystallographic Data Base [29] for those structures containing a Me$_3$Si–CH$_2$ moiety. These structural effects, are consistent with contributions of the quinonoid reso-

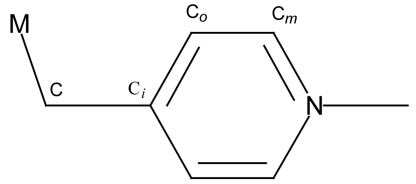


Scheme 2.

Table 1
Crystal data and structure refinement for **8**·triflate and **12**·tosylate

Empirical formula	$C_{10}H_{18}NSi^+ \cdot CF_3SO_3$	$C_7H_{10}N^+ \cdot C_7H_7SO_3^-$
Formula weight	329.41	279.35
Temperature (K)	130.0(2)	130.0(2)
Wavelength (Å)	1.54180	0.71069
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	$P2_12_12_1$
Unit cell dimensions		
a (Å)	28.186(2)	6.3612(1)
b (Å)	8.635(1)	8.503(1)
c (Å)	6.690(3)	25.925(2)
V (Å^3)	1628.3(8)	1402.4
D_{calc} (Mg m^{-3})	1.344	1.323
Z	4	4
$F(000)$	688	592
Crystal size (mm)	0.38 × 0.30 × 0.12	0.3 × 0.2 × 0.08
θ range for data collection (°)	3.14–69.8	2.52–29.91
Limiting indices	$0 \leq h \leq 34$, $0 \leq k \leq 10$, $-8 \leq l \leq 0$	$-7 \leq h \leq 8$, $-10 \leq k \leq 11$, $-30 \leq l \leq 33$
Reflections collected/unique	1655/1655 [$R_{int} = 0.0000$]	4908/3317 [$R_{int} = 0.0223$]
Completeness to theta	69.88, 99.9%	29.91, 98.6%
Max/min transmission	0.73, 0.45	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1655/0/145	3317/0/174
Weighting scheme	$w = 1/[\sigma2(Fo2)+(A*P)2+B*P]$, where $P = (Fo2+2Fc2)/3$ A = 0.0543 B = 1.2339	A = 0.0517 B = 0.6586
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0358$, $wR_2 = 0.0995$	$R_1 = 0.0394$, $wR_2 = 0.0962$
R indices (all data)	$R_1 = 0.0383$, $wR_2 = 0.1018$	$R_1 = 0.0469$, $wR_2 = 0.1002$
Absorption correction	Analytical	None
Extinction coefficient	0.0005(2)	0.0016(12)
Goodness-of-fit on F^2	1.057	1.003
Largest difference peak and hole (e Å^{-3})	0.396 and −0.364	0.441 and −0.427

Table 2
Selected bond distances and angles for compounds **8** and **12**



8·triflate	**12**·tosylate	
C–C$_i$	1.486(3)	1.502(3)
C$_i$–C$_o$	1.398(2)	1.388(3), 1.389(3)
C$_o$–C$_m$	1.367(3)	1.372(3), 1.376(3)
C$_m$–N	1.349(2)	1.351(3), 1.344(3)
N–Me	1.474(3)	1.475(2)
Si–CH$_2$	1.895(3)	
Si–Me(av.)	1.855	
Si–CH$_2$–C$_i$	113.9(2)°	
Si–CH$_2$–C$_i$–C$_o$	88.8(2)°	

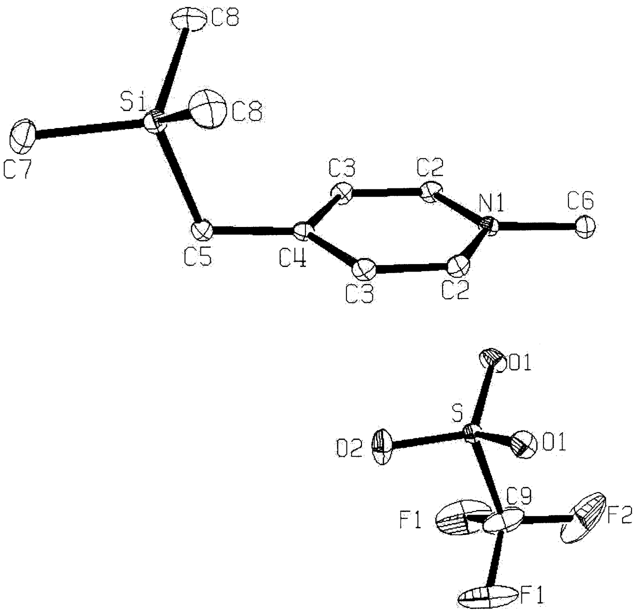
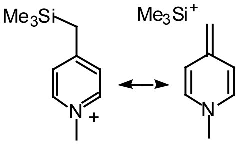


Fig. 1. Thermal ellipsoid plot of **8**·triflate. Ellipsoids are at the 20% probability level.

nance form **8′** to the ground state structure of **8**.



8 **8'**

To further characterise the structural effects of hyperconjugation in **8** and in the parent system **9** the ^{29}Si–^{13}C and ^{13}C–^{13}C one-bond coupling constants were determined, the coupling constants measured for **8** and **9** in addition to those previously reported [22] for compounds **13**–**16** are presented in Table 3.

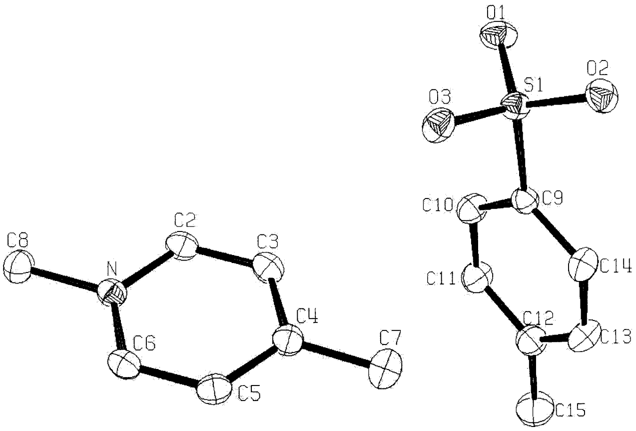
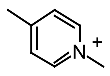
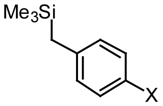


Fig. 2. Thermal ellipsoid plot of **12**·tosylate. Ellipsoids are at the 20% probability level.



12



13; X = OMe
14; X = Me
15; X = H
16; X = CN

The effects of hyperconjugation in benzylsilanes has been shown to decrease the Si–C one-bond coupling constant, the magnitude of the effect depending on the electron demand of the aromatic ring system. Thus Lambert [22] demonstrated that the Si–CH$_2$ coupling constant decreased from 46.9 Hz in 4-methoxybenzylsilane **13** down to 43.8 in 4-cyanobenzylsilane **16**, consistent with the higher electron demand in the cyano derivative **16**. The ^{29}Si–^{13}C coupling constant was determined to be 41.8 Hz for the parent pyridine system **9** this value is smaller than that observed for **16** consistent with stronger hyperconjugation in **9** than in **16**, this result suggests that a 4-substituted pyridine ring has a higher greater electron demand than a 4-substituted benzonitrile. Methylation of **9** giving the charged pyridinium ring in **8** resulted in a decrease in the ^{29}Si–^{13}C coupling constant down to 35.9 Hz reflecting as expected for the more strongly electron demanding aromatic ring in **8**. The effects of the

Table 3
One bond couplings for compounds **8**, **9** and **13**–**14** [22]

	Me–Si	Si–CH$_2$	CH$_2$–C$_i$	C$_i$–C$_o$	C$_o$–C$_m$
8	52.7	35.9	39.7	52.9	61.1
9	51.9	41.8	40.2	54.3	58.7
13′	51.3	46.9	41.4	57.3	58.6
14	51.3	46.5	41.1	56.8	57.2
15	51.4	46.1	40.9	56.5	56.8
16	51.8	43.8	40.3	55.9	58.0

stronger hyperconjugation in **8** are also apparent in the magnitudes of the $^{13}C-^{13}C$ one bond coupling constants within the pyridine ring, thus methylation of **9** results in a decrease in the C_i-C_o from 54.3 to 52.9 Hz and an increase in the C_o-C_m from 58.7 to 61.1 Hz reflecting the greater contribution of the resonance form **8′** to the ground state structure of **8**. The CH_2-C_i coupling constant is not sensitive to the effects of hyperconjugation, this has been observed previously [30].

2. Conclusion

Solid state and solution evidence for the presence of strong hyperconjugation (σ–π conjugation) between the CH_2-Si σ bonding orbital and the charged pyridinium π system has been demonstrated.

3. Experimental

3.1. X-ray structure determinations

Data were collected on an Enraf Nonius CAD-4Machs single crystal diffractometer in the $\omega-2\theta$ scan mode K. The temperature was maintained at 130.0(2) during the data collections using an Oxford Cryostream cooling device. Solution by direct methods (SHELXS-86) [31] and refinement using SHELXL-97 [32]. Thermal ellipsoid plots were generated by the program ORTEP 3 [33], within the WINGX [34] suite of programs.

General experimental details have been published in a previous paper [26].

3.2. Preparation of 4-trimethylsilylmethylpyridine (*9*)

A solution of 4-picoline (5.3 g, 0.056 mol) in ether (50 ml) was treated with a solution of methyllithium (1.4 M 1.05 equivalents) and heated to reflux for 30 min. Upon cooling the resulting slurry was carefully pippetted into a solution of chlorotrimethylsilane (1.5 equivalents) in ether (50 ml). The resulting mixture was stirred for 30 min then quenched by the addition of water. The ether layer was separated, washed with water (2 × 50 ml) dried ($MgSO_4$) and evaporated down to a pale yellow oil (8.1 g) 86% ^1H-NMR: δ ($CDCl_3$) 8.21 (2H, d, $J = 5.5$ Hz), 6.73, (2H, d, $J = 5.5$ Hz), 1.9 (2H, s), −0.17 (9H, s). ^{13}C-NMR: δ ($CDCl_3$) 149.8 (C_i), 148.8, 123.1, 26.9, −2.45.

3.3. Preparation of methyl 4-trimethylsilylpyridinium iodide (*8*·iodide)

A solution of **9** (100 mg) in deuterochloroform (0.5 ml) was treated with methyl iodide (1.1 equivalents), after 24 h the ^1H- and ^{13}C-NMR signals characteristic of **9** had disappeared and were replaced by those of **8**.^1H-NMR δ 8.6 (2H), 7.18 (2H), 4.05 (3H), 2.15 (3H), −0.21 (9H) ^{13}C-NMR: δ 161.7, 142.4, 124.8, 46.5, 29.1, −3.3.

3.4. Preparation of N-methyl 4-trimethylsilylpyridinium triflate (*8*·triflate)

A solution of **9** (100 mg) in deutero acetonitrile (0.5 ml) was treated with neat methyl triflate (1.05 equivalents). The resulting solution was left at 0° overnight whereupon large colourless blocks of (**8**·triflate) m.p. 192–193 (d) suitable for X-ray analysis had formed.

3.5. Preparation of N-methyl 4-picolinium tosylate

A solution of 4-picoline (0.5 g, 0.0054 mol)) in diethylether (20 ml) was treated with a solution of methyltosylate (1.1 g, 0.0059 mmol) in diethylether 95 ml). After leaving for 24 h the resulting precipitate was filtered. Recrystallisation from methanol–diethylether gave **12**·tosylate as thick plates, m.p. 152–153°.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 184367 and 184368 for compounds **8**·triflate and **12**·tosylate. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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