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Nita Sahai* and John A. Tossell: ^{29}Si NMR Shifts and Relative Stabilities Calculated for Hypercoordinated Silicon–Polyalcohol Complexes: Role in Sol–Gel and Biogenic Silica Synthesis

Pages 750−755. Minus signs are missing from many values in Tables 1−4, and some of the formulas in these tables are incorrect. The correct tables are presented here.

Page 750. In the right-hand column of text, in the second new paragraph, the formula referring to Figure 1e should be $[(C_2H_4O_2)_5{}^{P}Si_2]^{2-}$.

Page 751. In the left-hand column of text, in the first new paragraph, the formula referring to Figure 1d should be $[(C_2H_4O_2)_3{}^{P}SiH]^{-}$ and the formula referring to Figure 1f should be $(C_2H_4O_2)_3{}^{Q}SiH_2$. In the right-hand column of text, the formula referring to Figure 2e should be $[C_4H_8O_3(OH){}^{Q}Si(OH)_3]$ and the shift value for Figure 2f should be −73.8 ppm.

Page 752. The formula in Figure 1a should be $[(C_4H_8O_4)_2{}^{Q}Si]$, the formula in Figure 1e should be $[(C_2H_4O_2)_5{}^{P}Si_2]^{2-}$, and the formula in the caption for Figure 1f should be $[(C_2H_4O_2)_3{}^{Q}SiH_2]$.

Page 753. In the left-hand column of text, the formula referring to Figure 2j should be $[C_4H_8O_4{}^{H}Si(OH)_4]^{2-}$.

Page 754. The formula in the caption for Figure 2j should be $[C_4H_8O_4{}^{H}Si(OH)_4]^{2-}$.

Page 755. In footnote 40, the correct spelling of the second author's last name is Pfleiderer.

Table 1. Comparison of NMR Shifts Calculated for Geometries Optimized in the Gas-Phase and in Continuum Media Representing Water and Toluene[a]

	δ_{calc} (ppm)		
model complex	gas phase	SCRF water ($\epsilon = 78.5$)	SCRF toluene ($\epsilon = 2.379$)
$(C_2H_4O_2)_2{}^{Q}Si$	−44.0	−44.0	−44.0
$(C_3H_6O_3)_2{}^{Q}Si$	−83.4	−82.5	−83.0
$(C_4H_8O_4)_2{}^{Q}Si$	−75.0	−74.0	−74.0
$[C_2H_4O_2{}^{P}Si(OH)_3]^{-}$	−116.2	−116.9	−117.7
$[C_4H_8O_4{}^{P}Si(OH)_3]^{-}$	−129.2	−128.3	−128.8

[a] SCRF represents the Onsager self-consistent reaction field continuum solvation model.

Table 2. ^{29}Si NMR Isotropic Shifts and Anisotropic Shifts ($|\sigma_{33} - \sigma_{11}|$) Reported in Parts per Million with Respect to TMS Standard, for Silicon−Polyalcohol Spirocyclic Complexes[a]

model complex	ligand: Si ratio	δ_{expt}	δ_{calc}, HF/6-311+G(2d,p)	δ_{calc}, B3LYP/6-311+G(2d,p)	$\lvert\sigma_{33} - \sigma_{11}\rvert$,[b] HF/6-311+G(2d,p)
Effect of Ring Size, ^{Q}Si					
$(C_2H_4O_2)_2{}^{Q}Si$	2:1	-43.6^{c}	−44.0	−42.2	46.9
$(C_3H_6O_3)_2{}^{Q}Si$	2:1	-81.7^{c-e}	−83.4	−83.4	31.7
$(C_4H_8O_4)_2{}^{Q}Si$	2:1	$-81.6^{c,e}$	−75.0	−75.0	8.8
Effect of Ring Size and Hypercoordination, ^{P}Si					
$[(C_2H_4O_2)_2{}^{P}SiOH]^{-}$	2:1	-102.7^{e}	−108.9	−100.3	102.7
$[(C_3H_6O_3)_2{}^{P}SiOH]^{-}$	2:1	-130.4^{e}	−140.3	−144.1	133.9
$[(C_4H_8O_4)_2{}^{P}SiOH]^{-}$	2:1	$-130.8, -131.1^{e}$	−133.3	−133.6	127.9
Effect of Decreasing Ligand:^{P}Si Ratio at Fixed Ring Size					
$[(C_2H_4O_2)_3{}^{P}SiH]^{-}$	3:1	$-103, -104, -105^{f}$	−110.2		81.7
$[(C_2H_4O_2)_5{}^{P}Si_2]^{2-}$	5:2	$-103, -104, -105^{f}$	−114.4, −114.4		76.8, 90.9
Effect of Protonating an O_{br}[g]					
$[(C_2H_4O_2)_3{}^{P}SiH_2]_{bidentate} \rightarrow$ $[(C_2H_4O_2)_3{}^{Q}SiH_2]_{monodentate}$	3:1		−64.7		33.2
Standard					
$^{Q}Si(CH_3)_4$ (TMS)			0.0 ($\sigma = 386.0$)	0.0 ($\sigma = 327.9$)	0.0

[a] Geometries were obtained at the HF/6-31G* level. Experimental values for isotropic shifts are included for error estimation on our calculated values. [b] Anisotropic shifts reported are the absolute value of the difference between the maximum and the minimum eigenvalues of the shielding tensor. [c] Reference 35. [d] Assigned to polymeric Si spirocyclic complex in ref 35. [e] Values for the analogous dialato complexes. [f] Reference 21. [g] O_{br} represents a bridging oxygen.

Table 3. ^{29}Si HF/6-311+G(2d,p) NMR Isotropic Shifts and Anisotropic Shifts ($|\sigma_{33} - \sigma_{11}|$) Reported with Respect to TMS Standard, for Silicon−Polyalcohol Monocyclic Complexes[a]

model complex	δ (ppm)	$\lvert\sigma_{33} - \sigma_{11}\rvert^{b}$ (ppm)
Effect of Ring Size, ^{Q}Si		
$C_2H_4O_2{}^{Q}Si(OH)_2$	−57.2	24.5
$C_3H_6O_3{}^{Q}Si(OH)_2$	−77.0	42.5
$C_4H_8O_4{}^{Q}Si(OH)_2$	−75.2	35.6
$C_4H_{10}O_4 \cdots {}^{Q}Si(OH)_4$	−71.2	22.0
Effect of Ring Size and Hypercoordination		
$[C_2H_4O_2{}^{P}Si(OH)_3]^-$	−116.9	130.6
$[C_3H_6O_3{}^{P}Si(OH)_3]^-$	−130.4	139.0
$[C_4H_8O_4{}^{P}Si(OH)_3]^-$ (**I**) Si bonded to O on C_1, C_4	−128.3 [c]	140.8
$[C_4H_8O_4{}^{P}Si(OH)_3]^-$ (**II**) Si bonded to O on C_1, C_2	−117.3	124.4
$[C_5H_{10}O_5{}^{P}Si(OH)_3]^-$	−128.0	137.5
$[C_4H_8O_4{}^{H}Si(OH)_4]^{2-}$ hexacoordinated Si	−179.9 [d]	8.4
Effect of Protonating an O_{br}		
$C_2H_4O(OH){}^{P}Si(OH)_3$ (bidentate) → $C_2H_4O(OH){}^{Q}Si(OH)_3$ (monodentate)	−75.0	14.3
$[C_4H_8O_3(OH){}^{P}Si(OH)_3]$ (**I**, bidentate) → $[C_4H_8O_3(OH){}^{Q}Si(OH)_3]$ (**I**, monodentate)	−75.2	21.7
$[C_4H_8O_3(OH){}^{P}Si(OH)_3]$ (**II**, bidentate) → $[C_4H_8O_3(OH){}^{Q}Si(OH)_3]$ (**II**, monodentate)	−73.8	17.3
Effect of Chelate Denticity		
$[C_4H_7O_4{}^{P}Si(OH)_2]^-$ Si bonded to O on C_1, C_2, C_4 (tridentate ligand)	−122.4	101.7
Effect of Polymerization, ^{Q}Si and ^{P}Si		
$(C_3H_6O_2)_3{}^{Q}Si_3O_3$	−96.9	32.8
$[(C_3H_6O_2)_3{}^{Q}Si_2O_2{}^{P}SiO(OH)]^-$	−87.5, −90.3, −143.1 (mean = −107.0)	61.1, 97.2, 42.6
Standard		
${}^{Q}Si(CH_3)_4$ (TMS)	0.0 ($\sigma = 386.0$)	0.0

[a] Geometries were obtained at the HF/6-31G* level. [b] Anisotropic shifts reported refer to the absolute value of the difference between the maximum and the minimum eigenvalues of the shielding tensor. [c] This structure was proposed to explain a ^{29}Si resonance seen at −102 to −103 ppm in an experimental study of aqueous silicon−polyalcohol solutions.[22] [d] This structure was proposed to explain a ^{29}Si resonance seen at −145 to −147 ppm.[22]

Table 4. Reaction Energies (kcal mol^{-1}) for Polyol−Silicate Complex Formation, at the HF/6-31G* Level in the Gas Phase and in a SCRF Representing Solvation[a]

no.	reaction	ΔE_r, gas	$\Delta H^0{}_{r,gas} = \Delta E_{r,gas} + \Delta H_{therm}$	$\Delta E_{r,SCRF}$	$\Delta H^0{}_{r,SCRF} = \Delta E_{r,SCRF} + \Delta H_{therm}$
1	$C_4H_{10}O_4 + Si(OH)_4 = C_4H_{10}O_4 \cdots {}^{Q}Si(OH)_4$	−8.91 (−7.34)	−7.78 (−6.21)	−9.10 (−7.53)	−7.97 (−6.40)
2	$C_4H_{10}O_4 + Si(OH)_4 = C_4H_8O_4{}^{Q}Si(OH)_2 + 2H_2O$	+6.59	+5.96	−11.99	−12.61
3	$C_4H_{10}O_4 + Si(OH)_4 = [C_4H_8O_4{}^{P}Si(OH)_3]^- + H_2O + H^+$	+354.84	+351.14	+33.26	+29.56
4	$C_4H_{10}O_4 + Si(OH)_3O^- = [C_4H_8O_4{}^{P}Si(OH)_3]^- + H_2O$	−13.18	−11.36	−21.15	−19.33

[a] Values in parentheses are corrected for basis set superposition error (BSSE). BSSE and thermal contributions were estimated elsewhere.[30] (1 Hartree = 627.6 kcal mol^{-1}.)

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