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Identification and quantification of *cis* and *trans* isomers in aminophenyl double-decker silsesquioxanes using ^{1}H–^{29}Si gHMBC NMR

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***Cis* and *trans* isomers of a series of double-decker silsesquioxanes (DDSQ) were characterized by two-dimensional NMR techniques. The ^{1}H NMR spectra of these species have not previously been assigned to a degree that allows for quantification. Thus, ^{1}H–^{29}Si HMBC correlations were applied to facilitate ^{1}H spectral assignment and also to confirm previous ^{29}Si assignments for this class of silsesquioxanes. With the ability to identify all the pertinent resonances of the ^{1}H NMR spectrum, ^{29}Si NMR is no longer required for quantification and required only for characterization. This not only saves time and material but also provides a more accurate quantification, thus allowing for the ratio of *cis* and *trans* isomers present in each compound to be determined. A more accurate measure of the *cis*/*trans* ratio enables the investigation of its influence on the physical and chemical properties of DDSQ nanostructured materials. Copyright © 2013 John Wiley & Sons, Ltd.**

Keywords: NMR; ^{1}H; ^{29}Si; 2D NMR; ^{1}H–^{29}Si HMBC; double-decker silsesquioxanes; *cis*/*trans* isomers

Introduction

Inorganic–organic nanostructured molecules combine the thermostability of inorganics with the chemical flexibility of organics, thereby providing a versatile platform that has attracted attention over the last two decades.[1–11] A recently developed platform known as double-decker silsesquioxanes (DDSQ) (e.g. **3**) provides a unique opportunity to investigate the influence of stereo-configurations on the physical and chemical properties of silsesquioxanes. DDSQ are composed of two 'decks' of silsesquioxanes stacked on top of one another forming a cage-like structure.[12–19] Typically, the DDSQ (**3**) are synthesized through reacting a dichlorosilane with a tetrasilanol (**2a**) which generates both *cis* and *trans* isomers. DDSQ with various chemical moieties, including aminophenyls, and 2-methylpropyl-hydroxyl have been synthesized, and their *cis* and *trans* isomers have been partially isolated.[14,15] These isomers have been identified using one-dimensional (1D) ^{29}Si NMR spectroscopy.[14–19] While ^{29}Si NMR does benefit from large chemical shift dispersion typically leading to reduced spectral congestion, the technique is not ideal.[20] ^{29}Si NMR delivers lower relative sensitivity when compared to that of ^{1}H NMR; it also requires a longer recycle delay and experimental time for quantitative measurements, more concentrated samples, and a broadband probe with appropriate hardware (i.e. broadband amplifier, RF filters, and specific capacitor sticks for tuning) for accurate results. These factors make ^{29}Si NMR less desirable when compared to the high sensitivity, shorter relaxation and acquisition times, more dilute samples, and standard NMR equipment required for ^{1}H NMR. The ability to identify the isomeric ratio of DDSQ molecules using ^{1}H NMR spectroscopy would save time and material and ultimately provide a more accurate quantification of the isomeric ratio than utilizing ^{29}Si NMR spectroscopy. In this work, the ^{1}H NMR spectra of *cis* and *trans* isomers of [(meta- and para-aminophenyl)methylsilyl]-bridged-(phenyl)$_8$-double-decker silsesquioxane, DDSQ(m/p-AP)(Me), and [(meta-aminophenyl) cyclohexylsilyl]-bridged-(phenyl)$_8$-double-decker silsesquioxane, DDSQ(m-AP)(Cy), are assigned, and their ratios are quantified. In order to unambiguously assign the proton resonances and use them for quantitation, two-dimensional (2D) NMR techniques were necessary. Specifically, proton correlations to the silicon nuclei of the silsesquioxane core not only facilitated ^{1}H spectral assignment but also confirmed previous ^{29}Si assignments for this class of DDSQ.

Results and Discussion

DDSQ(m/p-AP)(Me) and DDSQ(m-AP)(Cy) were synthesized according to a previously described method (Scheme 1, Fig. 1) and produced a nearly equivalent mixture of *cis* and *trans* isomers.[15] The isomeric mixture of each compound was assessed by ^{29}Si and ^{1}H NMR, and diagnostic chemical shifts for each isomer were observed in the spectra.[15] The isomeric mixture of DDSQ(m-AP)(Me) (**3a**) shows the expected ^{29}Si resonances at δ –30.6, –78.4, –79.4, –79.6, and –79.8 in a ratio of 2:4:1:2:1 (Fig. 2a). *Trans* DDSQ(m-AP)(Me) (*trans* **3a**) shows characteristic ^{29}Si resonances at δ –30.6, –78.4, and –79.6 in the ratio of 2:4:4 (Fig. 2b), and *cis* DDSQ(m-AP)(Me)-isomer (*cis* **3a**) has ^{29}Si resonances at δ –30.6, –78.4, –79.4, and –79.8 in a ratio of 2:4:2:2 (Fig. 2c).[15] The ^{29}Si resonance at δ –30.6 has been assigned to the D-group silicon atoms (Si-3), silicon atoms bonded to two oxygen atoms (Fig. 1).[21] The ^{29}Si resonance at δ –78.4 has been

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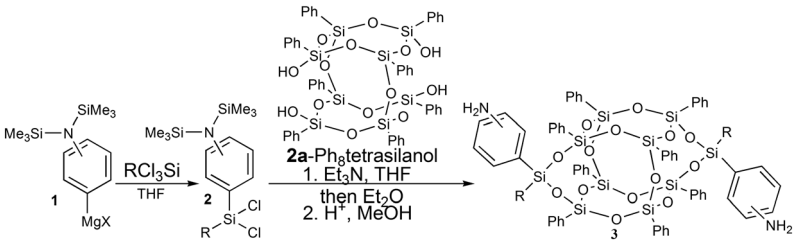

Scheme 1. Synthesis of DDSQ(m/p-AP)(R); X = Cl, Br; R = Me, Cy.

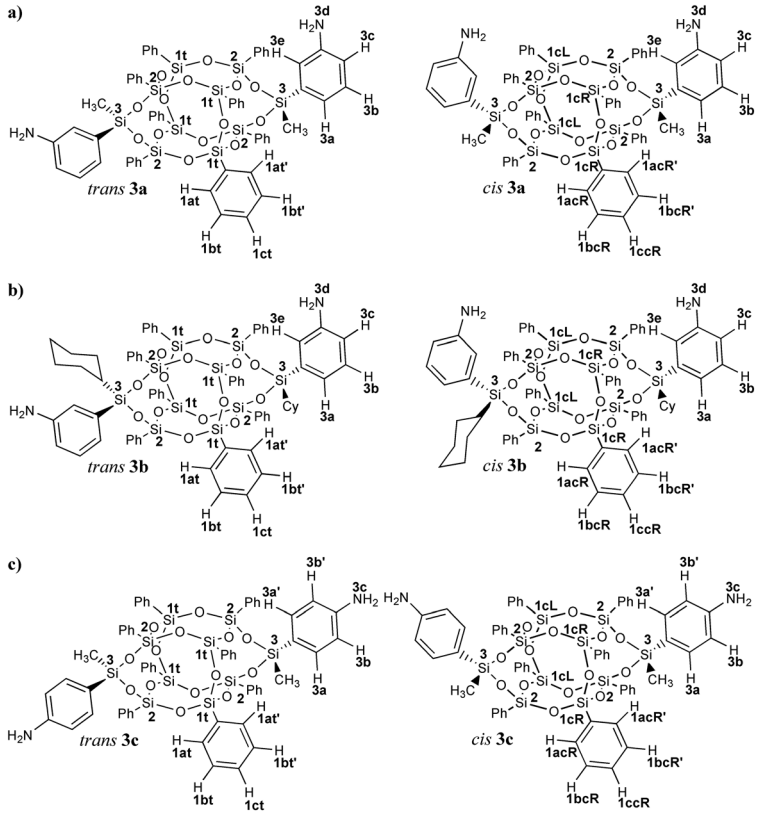

Figure 1. (a) *cis/trans* **3a**: DDSQ(m-AP)(Me), (b) *cis/trans* 3**b**: DDSQ(m-AP)(Cy), and (c) *cis/trans* **3c**: DDSQ(*p*An)(Me).

assigned to the T-group silicon atoms, silicon atoms bonded to three oxygen atoms, nearest to the D-group silicon atoms (Si-2). ^{29}Si resonances at δ –79.4, –79.6, and –79.8 have been assigned to the internal T-group silicon atoms, Si-1cR, Si-1t, and Si-1cL, respectively. Each Si-1t has the same chemical environment with proximity to one methyl and one aminophenyl group, giving rise to a single silicon resonance. In contrast, Si-1cR atoms are only proximal to the methyl group and Si-1cL to the aminophenyl group, thereby leading to two resonances. The ^{29}Si resonances for DDSQ(m-AP)(Cy) (**3b**) and DDSQ(p-AP)(Me) (**3c**) are nearly identical: δ –34.1, –78.5, –79.32, –79.5, and –79.7 (Fig. 2d), and δ –29.7, –78.2, –79.1, –79.3, and –79.5 in the ratio of 2:4:1:2:1 (Fig. 2e), respectively.

The ^{1}H NMR spectra for these DDSQ derivatives reveal that the proton resonances in the phenyl region (6.5–8 ppm) are the best candidates for the quantitation of isomeric ratios (Fig. 3). Proton signals belonging to the R-substituents (Me or Cy) proved to be ambiguous when attempting to decipher between *cis* and *trans* isomers. First, the proton signals belonging to the cyclohexyl groups are broad, significantly overlapped, and have complicated coupling patterns for *cis* and *trans* isomers. The proton signals belonging to the methyl groups of each isomer are broad singlets and overlap, making it difficult to integrate the individual peaks in this region. Secondly, the ^{29}Si signals associated with both organic R-groups (Me and Cy), as evidenced by ^{1}H–^{29}Si gradient-enhanced HMBC (gHMBC) cross-peaks, are isochronous for *cis* and *trans* isomers. This makes it impossible to use the previously established ^{29}Si shift assignments to determine the *cis* and *trans* proton signals in these regions, even if the signals were deconvoluted.

Compound 3a

The proton resonance at δ_H 7.54 was assigned to H-2a and H-2a′ (m, 16H) based on the gHMBC three-bond correlation with the ^{29}Si single resonance at δ_{Si} –78.4 (Si-2), which is isochronous for

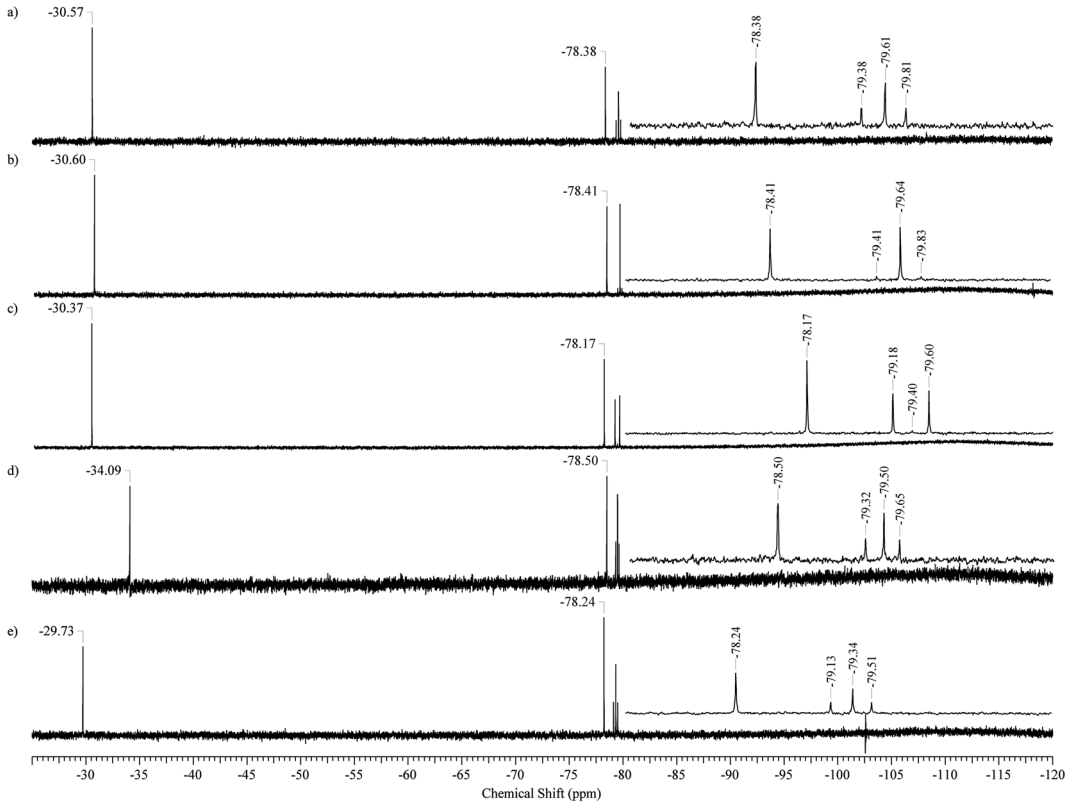

Figure 2. ^{29}Si NMR spectra of (a) *cis/trans* **3a**, (b) majority *trans* **3a**, (c) majority *cis* **3a**, (d) *cis/trans* **3b**, and (e) *cis/trans* **3c**.

both *cis* and *trans* isomers (Fig. 4a). Whereas the *trans* isomer exhibits a single resonance for Si-1t (δ_{Si} –79.6), the *cis* isomer, due to its asymmetry, has two pairs of Si-1 atoms, labeled Si-1cL (left) and Si-1cR (right) (δ_{Si} –79.4 and –79.8 in a ratio of 2:2). The proton multiplet at δ_H 7.48 was assigned to H-1acR and H-1acR′ (*cis*, m, 4H) as evidenced by the gHMBC correlation with the two Si-1cR atoms (δ_{Si} –79.8). The proton multiplet at δ_H 7.16 was also assigned to H-1acL and H-1acL′ (*cis*, m, 4H) based on the gHMBC correlation with the two Si-1cL atoms (δ_{Si} –79.4). For the *trans* isomers, the proton multiplet at δ_H 7.32 was assigned to H-1at and H-1at′ (*trans*, m, 8H), which is confirmed by the gHMBC correlation with the Si-1t atoms (δ_{Si} –79.6). Both the *cis* and *trans* isomers show isochronous resonances at δ_H 6.92 and 7.03 and were assigned to H-3a and H-3e (m, 4H and m, 4*H*) based on the gHMBC correlation with the four Si-3 atoms (δ_{Si} –30.5). Analysis of the ^{1}H–^{1}H gradient-enhanced COSY (gCOSY) spectrum revealed that proton signals at δ_H 6.67 and 7.08 show correlations with δ_H 6.92 and 7.03, thereby establishing their assignment as H-3b and H-3d. Proton multiplets assigned to H-1acL and H-1acL′ (δ_H 7.16) and H-1at and H-1at′ (δ_H 7.32) exhibit too much overlap for accurate quantification. Thus, the proton resonances assigned to H-1acR and H-1acR′ (δ_H 7.48) and H-2a and H-2a′ (δ_H 7.54) are the best candidates for quantification. An equivalent ratio of the *cis* to *trans* isomers would therefore be represented by a ratio of 1:4 for these resonances. The remaining protons were identified by ^{1}H–^{1}H gCOSY cross-peaks and coupling patterns (Table 1a).

Compound 3b

The ^{1}H and ^{29}Si NMR spectra of **3b** show an analogous coupling pattern to that of **3a** with only a slight variation of chemical shifts. Additionally, the 2D ^{1}H–^{29}Si gHMBC is analogous to that of **3a** (Fig. 3d)

Compound 3c

Similar to compounds **3a** and **3b**, the proton resonance at δ_H 7.55 was assigned to H-2a and H-2a′ (m, 16H) based on the correlation with the ^{29}Si single resonance at δ_{Si} –78.2 (Si-2), isochronous for both *cis* and *trans* isomers (Fig. 4b). The proton multiplet at δ_H 7.50 was assigned to H-1acR and H-1acR′ (*cis*, m, 4H), as evidenced by the gHMBC correlation with the Si-1cR atoms (δ_{Si} –79.5). The proton multiplet at δ_H 7.19 was also assigned to H-1acL and H-1acL′ (*cis*, m, 4H) based on the gHMBC correlation with the other two Si-1cL atoms (δ_{Si} –79.1). For the *trans* isomers, the proton multiplet at δ_H 7.33 was assigned to H-1at and H-1at′ (*trans* , m, 8H) based on the gHMBC correlation with the Si-1t atoms (δ_{Si} –79.3). The proton multiplet at δ_H 6.53 (8H) was assigned to H-3a and H-3a′, as evidenced by the gHMBC correlation with the four Si-3 atoms, and is isochronous for *cis* and *trans* isomers. The assignment of H-3a and H-3a′ is unique to the para-structure (**3c**). All 8 H-3 protons that demonstrate a three-bond gHMBC correlation with the Si-3 atoms of **3c** (H-3a and H-3a′) are represented by a single multiplet. The same 8H-3 protons of the meta-species (**3a** and **3b**) are represented by two multiplets (H-3a, 4H and H-3e, 4H), due to the asymmetry inherent to the meta-structure. Analysis of the ^{1}H–^{1}H gCOSY spectrum reveals that proton signal at δ_H 6.53 shows correlations with δ_H 7.47 (H-3b and H-3b′; isochronous for *cis* and *trans*, m, 8H). However, also contrary to the ^{1}H NMR spectra of the meta-species, the proton multiplet assigned to H-3b and H-3b′ (δ_H 7.47) overlaps the proton multiplet assigned to H-1acR and H-1acR′ (δ_H 7.50), which was used for quantification of the isomeric ratio of the previous two compounds. Similar to compounds

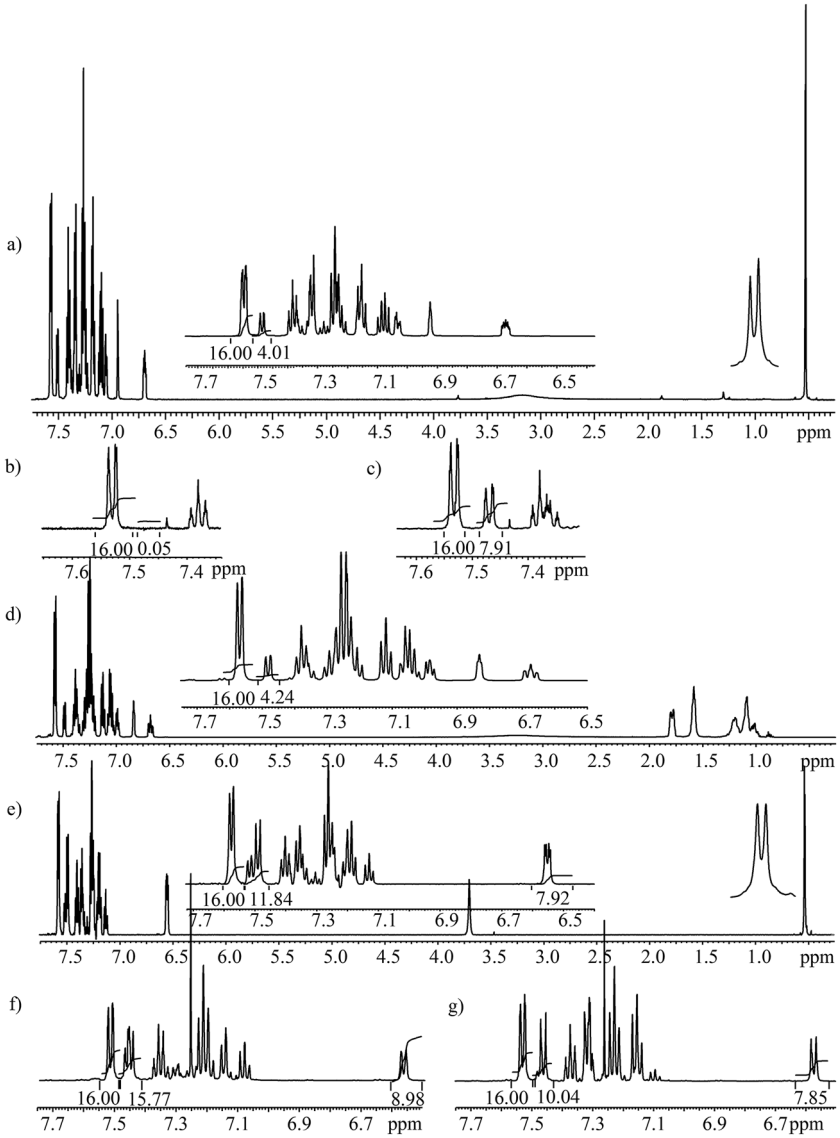

Figure 3. ^{1}H NMR spectrum of (a) *cis/trans* **3a**, (b) majority *trans* **3a**, (c) majority *cis* **3a**, (d) *cis/trans* **3b**, (e) *cis/trans* **3c**, (f) majority *trans* **3c**, and (g) majority *cis* **3c**.

3a and **3b**, the proton multiplets assigned to H-1acL and H-1acL′ (δ_H 7.19) and H-1act and H-1act′ (δ_H 7.33) exhibit too much overlap for accurate quantification, and to a much larger extent than the overlap of proton multiplets assigned to H-3b and H-3b′ (δ_H 7.47) and H-1acR and H-1acR′ (δ_H 7.50) (Fig. 3). Thus, the proton resonances assigned to H-2a and H-2a′ (δ_H 7.55) and H-1acR and H-1acR′ (δ_H 7.50), combined with H-3b and H-3b′ (δ_H 7.47), are still the best candidates for quantification. An equivalent ratio of the *cis* to *trans* isomers is represented by the proton signals at δ_H 7.50 and 7.47 integrating to 12H and the proton signal at δ_H 7.55 integrating to 16H, a ratio of 3:4. As the ratio of these signals increases, the ratio of isomers in the sample becomes majority *cis* **3c** (Figs 3e–3g). A ratio of 1:2 would signify an isolated *trans* **3c**. The remaining protons were identified by ^{1}H–^{1}H gCOSY cross-peaks and coupling patterns (Table 1b).

With the established ^{1}H NMR chemical shift assignments, integration was possible, and samples containing *cis* and *trans* isomers could be quantified (Table 2).

All quantitative ^{1}H were run with a sufficient recycle delay to allow for complete relaxation as determined by T_1 analysis. ^{29}Si NMR experiments were run with an empirically determined recycle delay of 12 s even though the T_1 values ranged from 50 to 55 s.[22] Determining the percentage of *cis* isomer present in samples of material **3c** was complicated by signal overlap around δ_H 7.50–7.47. For this system, it was necessary to subtract the integrated value of the protons at δ_H 6.60 (H-3b and H-3b′of *cis* **3c**) from that of δ_H 7.50–7.47 in order to determine the percentage of *cis* isomer.

For comparative purposes, the percentage of the *cis* isomer in various samples of **3a** was also determined using ^{29}Si NMR spectra and compared with their ^{1}H NMR counterparts (Table 3). Analysis times for ^{29}Si NMR spectra varied from 10 min to 12 h, while all ^{1}H NMR spectra were acquired in 13 min. Increasing the time of acquisition for the proton experiment did not lead to an appreciable change in calculated ratios. Contrariwise, as the length of analysis time for ^{29}Si NMR spectra was extended,

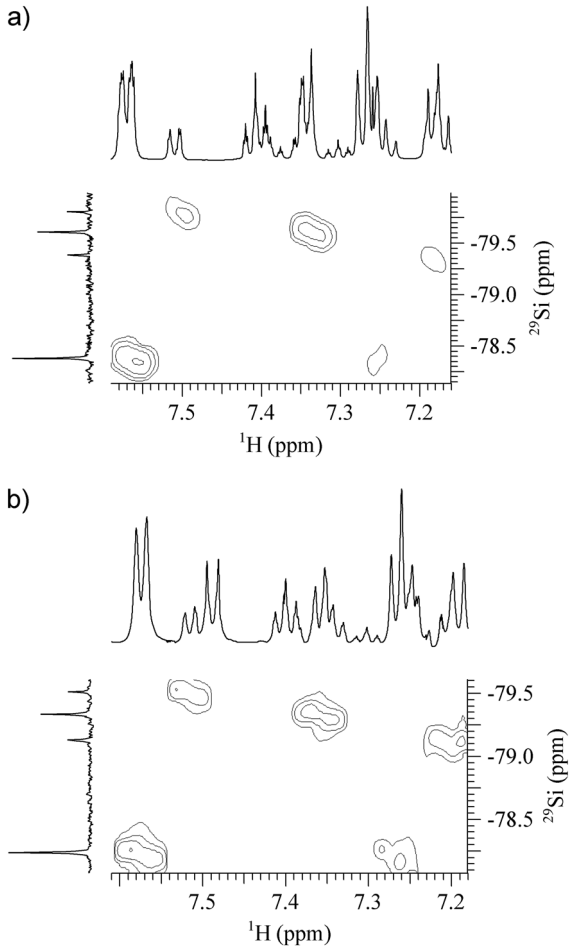

Figure 4. ^{1}H–^{29}Si gHMBC connectivity of (a) *cis/trans* **3a** and (b) *cis/trans* **3c**.

the percentage of *cis* isomer determined approached the percentages determined using the ^{1}H NMR spectra. No improvement was seen when extending ^{29}Si experiments past 4 h. The limiting factor was the poorer signal-to-noise (S/N) in the ^{29}Si NMR spectra. This not only made it more difficult to determine the limits of integration on ^{29}Si NMR spectra as compared to that of the ^{1}H NMR spectra but also increased the uncertainty in the former (Fig. 2). Even after 12 h, the S/N of the ^{29}Si NMR spectrum was not comparable to its ^{1}H NMR spectrum (Table 3), which was run for 13 min. For example, at 12 h, the S/N of the smallest signal integrated was 19:1, and the S/N of the largest integrated signal was 64:1 (exp 5-^{29}Si). The lowest and highest S/N for the ^{1}H NMR spectrum of the same material was 49:1 and 239:1, respectively (exp 5-^{1}H). For mixtures containing predominately one isomer, it becomes increasingly more difficult to accurately determine isomeric purity. As an example, after 4 h, the ^{29}Si NMR spectrum of a sample that is majority *cis* isomer had an S/N for the *trans* isomer signal of 2:1 while the S/N of the *cis* isomer signal was 34:1 (exp 4-^{29}Si). The signal representing the *trans* isomer could potentially be mistaken for, or hidden under, noise had the analysis time been shortened, the purity of the *cis* isomer increased, or the concentration of the sample decreased. All ^{29}Si samples had to be heavily concentrated, approximately 50 mg in 0.6 ml of solution, whereas the ^{1}H NMR spectra could be obtained with a concentration of < 5 mg in 0.6 ml of solution. Overall, more accurate data was acquired with ^{1}H NMR using less material and shorter analysis time.

Conclusion

In this study, ^{1}H–^{29}Si gHMBC and ^{1}H–^{1}H gCOSY were used to assign the chemical shifts of the protons for the *cis* and *trans* isomers of DDSQ(m/p-AP)(Me) and DDSQ(m-AP)(Cy) as well as to verify the chemical shifts of ^{29}Si NMR. Once the proton chemical shifts of these compounds were identified, a routine access methodology to determine the *cis* and *trans* isomeric ratio was developed. The method described herein offers a more accurate quantification of the isomeric ratio in a shorter analysis time using standard NMR equipment with less material required per sample when compared to utilizing ^{29}Si NMR spectroscopy. With the ability to identify the isomeric ratios, attempts to isolate the individual isomers can be made, and the influence of stereo-configurations on the physical and chemical properties of these hybrid nanostructured chemicals can be studied and utilized.

Experimental

Solvents and Reagents

Tricycle[7.3.3(3,7)]octasiloxane-5,14,17-tetraol-1,3,5,7,9,11, 14,17-octaphenyl (Ph_8tetrasilanol-POSS) was obtained from Hybrid Plastics (Hattiesburg, MS). Tetrahydrofuran (THF), hexanes, diethyl ether, magnesium turnings, triethylamine, trichloromethyl silane, and 3-[bis(trimethylsilyl)amino]phenyl-magnesium chloride were obtained from Sigma-Aldrich. The solvents used for synthesis were distilled under nitrogen and degassed using freeze–pump–thaw methods for synthetic procedures. All deuterated solvents were used as supplied by the vendor.

Synthesis

DDSQ(m/p-AP)(R) was synthesized based on a described method, except on a larger scale.[15]

Characterization

DDSQ(m/p-AP)(R) was measured at 25 °C on a Varian UNITY-Inova 600 spectrometer equipped with a 5-mm pulsed-field-gradient (PFG) switchable broadband probe and operating at 599.80 MHz (^{1}H) and 119.16 MHz (^{29}Si). 1D ^{1}H NMR data were acquired using a recycle delay of 20 s and 32 scans to ensure accurate integration. The pulse angle was set to 45°. The ^{1}H-chemical shifts were referenced to that of residual protonated solvent in $CDCl_3$ (7.24 ppm). 1D ^{29}Si{^{1}H} NMR data were acquired using a recycle delay of 12 s with inverse-gated decoupling. The pulse angle was set to 90°. ^{29}Si{^{1}H} spectra were referenced against the lock solvent using vendor-supplied lock referencing. All 2D NMR spectra were obtained using gradient pulses on a 5-mm PFG switchable broadband probe without sample spinning. Phase-sensitive spectra were acquired using the hyper-complex States method. Threefold linear prediction was applied to the *F*1 dimension as implemented by standard Varian software. ^{1}H-^{29}Si gHMBC

Table 1. ^{29}Si and ^{1}H resonances of (a) *cis/trans* **3a** and (b) *cis/trans* **3c**

Atom	^{1}H (mult.)	^{29}Si (mult.)
a		
1 (Si)	—	–79.4(2 Si)[a], –79.6(4 Si)[b], –79.8(2 Si)[a]
1-(C_6H_5)	—	—
-a,a′ (CH)	7.16(m, 4H)[a], 7.32(m, 8H)[b],7.48(m, 4H)[a]	—
-b,b′ (CH)	7.31(m, 4H)[a], 7.15(m, 8H)[b], 7.23(m, 4H)[a]	—
-c (CH)	7.39(m, 4H)[c], 7.38(m, 4H)[c], 7.25(m, 4H)[c], 7.10(m, 4H)[c]	—
2 (Si)	—	–78.4 (8 Si)[d]
2-(C_6H_5)	—	—
-a,a′ (CH)	7.54(m, 16H)[d]	—
-b,b′ (CH)	7.24(m, 16H)[d]	—
-c (CH)	7.39(m, 4H)[c], 7.38(m, 4H)[c], 7.25(m, 4H)[c], 7.10(m, 4H)[c]	—
3 (Si)	—	–30.6 (4 Si)[d]
3-(CH_3)	0.51 (s, 12H)[c]	—
3-(C_6H_6N)	—	—
-a (CH)	6.92 (m, 4H)	—
-b (NH_2)	3.16 (s, 8H)[d]	—
-c (CH)	6.67 (m, 4H)[d]	—
-d (CH)	7.08 (m, 4H)[d]	—
-e (CH)	7.03 (m, 4H)[d]	—
b		
1 (Si)	—	–79.1(2 Si)[a], –79.3(4 Si)[b], –79.5(2 Si)[a]
1-(C_6H_5)	—	—
-a,a′ (CH)	7.19(m, 4H)[a], 7.33(m, 8H)[b],7.50(m, 4H)[a]	—
-b,b′ (CH)	7.32(m, 4H)[a], 7.18(m, 8H)[b], 7.20(m, 4H)[a]	—
-c (CH)	7.39(m, 4H)[c], 7.38(m, 4H)[c], 7.25(m, 4H)[c], 7.11(m, 4H)[c]	—
2 (Si)	—	–78.2 (8 Si)[d]
2-(C_6H_5)	—	—
-a,a′ (CH)	7.55(m, 16H)[d]	—
-b,b′ (CH)	7.23(m, 16H)[d]	—
-c (CH)	7.39(m, 4H)[c], 7.38(m, 4H)[c], 7.25(m, 4H)[c], 7.10(m, 4H)[c]	—
3 (Si)	—	–29.7 (4 Si)[d]
3-(CH_3)	0.51 (s, 12H)[c]	—
3-(C_6H_6N)	—	—
-a,a′ (CH)	6.53 (m, 8H)[d]	—
-b,b′ (CH)	7.47 (m, 8H)[d]	—
-c (NH_2)	3.69 (s, 8H)[d]	—

[a]*cis*.
[b]*trans*.
[c]Cannot distinguish between *cis* and *trans*.
[d]Isochronous *cis/trans*.

Table 2. Integrated values of ^{1}H NMR spectra from various mixtures of **3**

Compound	δ_1	δ_2	Ratio	% *cis*
3a	0.05	16	3.13E–03	<1
	4.08	16	0.26	51
	7.91	16	0.49	99
3b	4.24	16	0.27	53
3c	12.35	16	0.77	50
	10.04	16	0.63	27
	15.77	16	0.99	85

Integrals are taken at the following δ and can be seen in Figure 3.
3a: $\delta_1 = 7.48$ ppm, $\delta_2 = 7.54$ ppm.
3b: $\delta_1 = 7.48$ ppm, $\delta_1 = 7.57$ ppm.
3a: $\delta_1 = 7.50 + 7.47$ ppm, $\delta_2 = 7.55$ ppm.

spectra were acquired with spectral widths of 6600 Hz and 14 370 Hz for *F*2 and *F*1, respectively.[23] The pre-acquisition delay was set to 1.0 s, and 400 increments with eight transients per increment containing 1069 data points were acquired. The three-bond J-filter was set to 7 Hz (Varian parameter; Jnxh = 7). Unshifted sine-bell windows, which were matched to the acquisition time, were used for processing both dimensions. Zero filling to 4096 data points was applied to *F*1 prior to 2D Fourier transformation. ^{1}H-^{1}H gCOSY spectra were obtained using a spectral width of 8000 Hz in both dimensions. The pre-acquisition delay was set to 1.0 s and 128 increments with four transients of 1152 data points were acquired. Both *F*2 and *F*1 were multiplied by unshifted sine-bell weighting functions that were matched to the acquisition or evolution time. Prior to 2D Fourier transformation, *F*2 and *F*1 were zero filled to 2048 and 1024 data points, respectively.

Table 3. Integrated values of ^{1}H NMR spectra *versus* ^{29}Si NMR spectra from various mixtures of **3a**

Exp #	Nucleus	Time	Ratio	% *cis*	S/N range (low–high)
1	^{29}Si	10 min	0.43	43	6–15
	^{1}H	13 min	0.26	51	57–183
2	^{29}Si	30 min	0.43	43	11–28
	^{1}H	13 min	0.25	49	52–201
3	^{29}Si	2 h	0.48	48	12–23[a]
	^{1}H	13 min	0.25	51	33–90
4	^{29}Si	4 h	0.97	97	2–34[b]
	^{1}H	13 min	0.49	99	91–149
5	^{29}Si	12 h	0.37	37	19–64
	^{1}H	13 min	0.2	39	49–239

^{29}Si: $\delta_1 = -79.4$ ppm, $\delta_2 = -79.6$ ppm, and $\delta_3 = -79.8$ ppm.

S/N = signal to noise.

[a]Effect of concentration.

[b]Lower peak is low-quantity *trans*.

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