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Note

Variable temperature ^1H and ^{29}Si NMR of diastereomeric 1,3-dihydroxy-1,3-bis[(2-dimethylaminomethyl)phenyl]-1,3-divinyldisiloxanes

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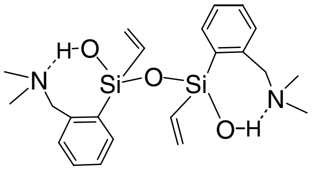
Abstract

Variable temperature NMR experiments of diastereomeric 1,3-dihydroxy-1,3-bis[(2-dimethylaminomethyl)phenyl]-1,3-divinyldisiloxanes, *meso*-**1** and *rac*-**1** having intramolecular hydrogen bondings were carried out. As temperature increased, the ^1H NMRs of hydroxy groups of **1** resulted in a low frequency and their ^{29}Si NMRs were very slightly shifted to a low frequency. Interestingly, the ^1H NMR of two benzylic protons was split more widely as temperature increased.

1. Introduction

It is an advantageous characteristic that most silanols have intra- or intermolecular hydrogen bondings. A variety of substituted silanols bearing intermolecular hydrogen bondings have been reported and the nature of the hydrogen bondings has been widely investigated [1–3]. Comparing to this, there have been fewer reports on the nature of intramolecular hydrogen bondings of silanols [4–9]. To date, there is no example of a detailed NMR study on the intramolecular hydrogen bonding of silanols. Recently, we reported diastereomeric silanols, 1,3-dihydroxy-1,3-bis[(2-dimethylaminomethyl)phenyl]-1,3-divinyldisiloxanes (**1**) having strong intramolecular hydrogen bondings between the hydroxy groups and the nitrogen atoms, evidenced by X-ray crystallographic analysis and ^1H NMR data [10]. Herein, we describe the variable temperature ^1H and ^{29}Si NMR of diastereomeric disiloxane-1,3-diols (**1**) showing a novel behavior for ^1H NMR of benzylic protons.



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2. Results and discussion

Diastereomeric compounds, **1** were prepared from the hydrolysis of (2-dimethylaminomethyl)phenylvinyldichlorosilane [11] bearing intramolecular coordination arms in the presence of Et_3N, as an HCl acceptor. *meso*-**1** and *rac*-**1** were able to be separated with forceps by virtue of their different crystal shapes [10].

In the variable temperature ^1H NMR spectra (in $CDCl_3$) of *meso*-**1** and *rac*-**1** [12], broad proton resonances caused by the hydroxy groups were observed at 9.90 and 9.98 ppm at room temperature, respectively. For the OH signal, a higher temperature led to a lower frequency shifted value. This reflects that a higher temperature weakens the intramolecular hydrogen bondings of silanols [13].

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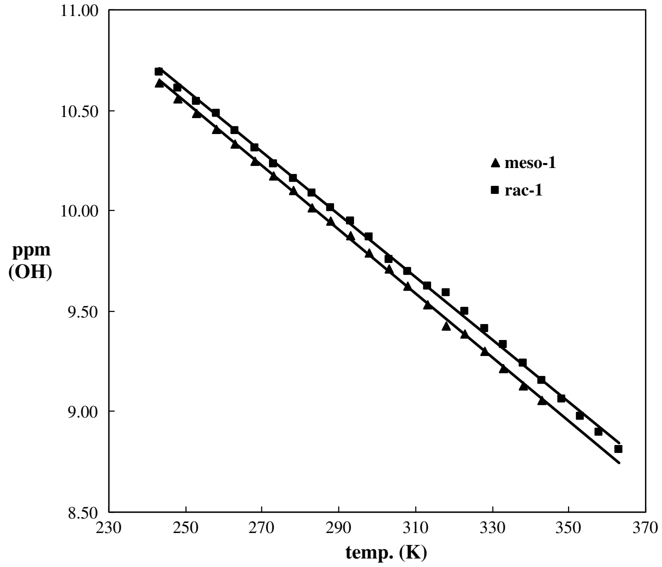

Fig. 1. Correlation between ^1H NMR shifts of OH and the temperatures.

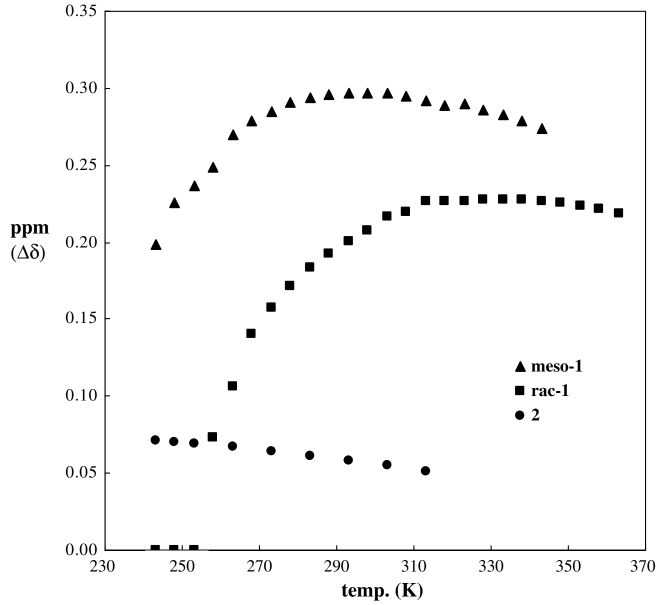

Fig. 3. Correlation between the $\Delta\delta$ of CH_2N and the temperatures.

The nearly linear correlation of temperatures vs. ^1H NMR chemical shifts of OH in *meso*-**1** and in *rac*-**1** is shown in Fig. 1.

The variable temperature ^1H NMR spectra of CH_2N for *rac*-**1** are shown in Fig. 2 exhibiting the diastereotopism of benzylic protons. Fig. 3 shows $\Delta\delta(=|\delta$ of benzylic H_a-δ of benzylic $H_b|)$ of *meso*-**1** and of *rac*-**1**. It should be noted that there is no change of coupling constants of geminal protons as the temperature increased. The resonances of CH_2N of *rac*-**1** were broad at 243 K, but were spilt at 258 K and higher as doublet–doublet patterns due to geminal couplings, which is an unexpected phenomenon. In general, the resonances of benzylic protons collapsed as the temperature increased due to the thermodynamic reasons [14–17]. To understand the unexpected phenomenon we assumed that a hydrogen bonding may play an important role in the resonances of benzylic protons. In order to exclude the influence of hydrogen bonding in the resonances of benzylic protons, 1,3-bis(trimethylsiloxy)-1,3-bis[(2-dimethylaminomethyl)phenyl]-1,3-divinyldisiloxane (**2**) in the absence of hydroxyl groups [18] was synthesized quantitatively by the reaction of *rac*-**1** with 2 equiv of trimethylchlorosilane in the presence of excess triethylamine in diethyl ether solvent. The ^1H NMR of CH_2N of **2** resulted in a typical pattern, showing that $\Delta\delta$ of **2** was decreased as the temperature increased [14–17], (Fig. 3) which was different from those of Fig. 2. This result indicates that the splitting patterns of benzylic protons of **1** shown in Fig. 2 resulted from the hydrogen bondings.

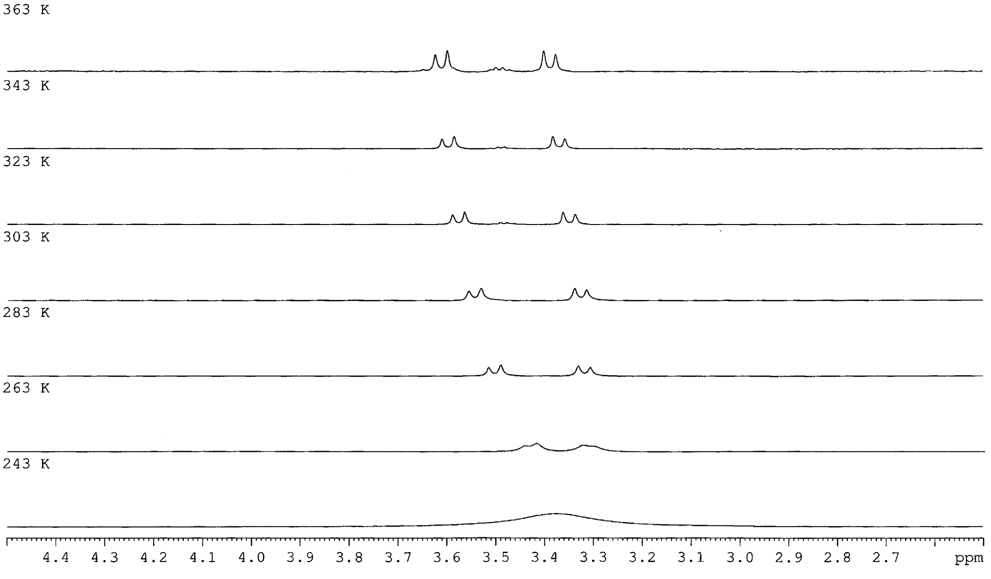

Fig. 2. Variable temperature ^1H NMR spectra of CH_2N for *rac*-**1**.

We could think of many considerations in order to understand the unexpected patterns. It is reasonable that this behavior such as increasing of chemical nonequivalency was derived from conformational changes and/or changes in structural rigidity around benzylic carbon. Our considerations are the following: (1) If the hydrogen bonding of **1** had become stronger as temperatures increased, this behavior would have been expected, but actually it became weaker as shown in Fig. 1. (2) It may be assumed that nitrogen atoms might be coordinated to Si atoms [14,15,19,20], because the hydrogen bonding was weakened as the temperature increased. However, this assumption could not be true based on ^{29}Si chemical shifts at variable temperatures (Fig. 4). Although the ^{29}Si chemical shifts of **1** resulted in a low frequency at a higher temperature, the degree of shifting between temperatures is almost negligible (about 0.3 ppm). This result suggests that there is no shielding of Si atoms by the coordination of nitrogen atom. (3) If the bond angle of the 7-membered ring involving hydrogen bonding is varied, the geminal coupling constant would also be varied. This supposition might be excluded due to the lack of change of the geminal coupling constant as mentioned above. (4) The equilibrium between diastereomeric isomers, **1** could not explain these phenomena since ^{1}H NMRs of isomers were distinguishable even at high temperature. (5) Two facts indicate dominant intramolecular hydrogen bondings at a high temperature (not intermolecular hydrogen bondings). First, the proton resonances of hydroxy groups were observed around 9 ppm at high temperature. Second, the ^{1}H and ^{29}Si chemical shifts were independent of sample concentrations. From the considerations mentioned above, we could think two plausible stages that (1) from 243 K to a lower temperature the coalescence (*rac*-**1**) might be triggered by usual site exchange of benzylic protons [14–17], and (2) the increment of $\Delta\delta$ over 243 K might be derived from newly developed intramolecular hydrogen bondings by a high temperature, such as intramolecular hydrogen bondings between hydroxy groups or between hydroxy group and other nitrogen atom in the same molecule. At this moment, its interpretation is open to speculation.

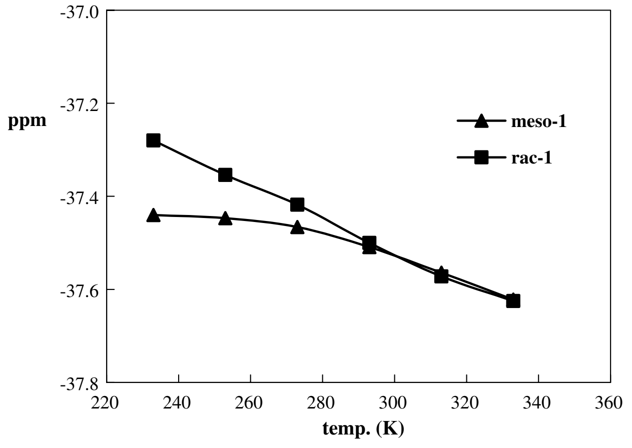

Fig. 4. Correlation between ^{29}Si NMR shifts and the temperatures.

In summary, variable temperature NMR experiments of diastereomeric disiloxane-1,3-diols, **1** having an intramolecular hydrogen bonding were carried out. As temperature increased, the ^{1}H NMRs of hydroxy groups of **1** resulted in a low frequency and their ^{29}Si NMRs were very slightly shifted to a low frequency. The ^{1}H NMR of two benzylic protons of **1** was split more widely in $CDCl_3$ solvent as temperatures increased.

Acknowledgements

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[18] 2: MS: *m*/*z* (relative intensity) 572 (M^+, 7.1), 557 (37.8), 514 (42.2), 438 (83.4), 278 (67.7), 145 (64.8), 159 (100), 58 (93.2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.14 (s, 18H, $SiMe_3$), 2.20 (s, 12H, $N(CH_3)_2$), 3.57 (doublet, $J = 14.0$ Hz, 2H, NCH_aH_b), 3.63 (doublet, $J = 14.0$ Hz, 2H, $NCH_a\ H_b$), 5.90–6.37 (m, 6H, $CH_2{=}CH$), 7.22–7.80 (m, 8H, C_6H_4). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 1.94 ($SiMe_3$), 45.30 (NMe_2), 63.53 (CH_2N), 125.72, 127.70, 130.78, 133.62, 130.74, 135.45, 135.85, 145.48 (vinyl and aryl). Anal. Calc. for $C_{28}H_{48}N_2O_3Si_4$: C, 58.69; H, 8.44; N, 4.89. Found: C, 58.65; H, 8.41; N, 4.91%.
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