Dynamics of Solvated Li^+ within *exo,exo*-[1,3-Bis(trimethylsilyl)allyl]lithium *N,N,N',N'*-Tetramethylethylenediamine Complex

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Abstract: The title compound **4**·TMEDA, prepared from 3-(trimethylsilyl)propene by a series of metalation (*sec*-butyllithium), silylation, and remetalation reactions, respectively, **1** → **2** → **3** → **4**, is revealed via ^{13}C and proton NMR, including a Saunders deuterium perturbation experiment, to be electronically symmetrical and exist in the exo–exo configuration. It is proposed that a small ^{13}C NMR shift (0.48 ppm) between C_1 and C_3 of allyl in **4**·TMEDA and a large shift between the two $(CH_3)_2N$ groups (4.65 ppm) are due to dissymmetry of solvation about lithium (one TMEDA and one diethyl ether) within the tight monomeric ion pair. Above 150 K there is signal averaging of the C_1 with C_3 resonances and of the peaks for $(CH_3)_2N$ in bound TMEDA. NMR line-shape analysis shows, most likely, all these spectral changes to be due to the same dynamic process, the rotation of the solvated Li^+ moiety with respect to the allylic loop. This rate of rotation is 300 s^{-1} at 160 K with $\Delta H^{\ddagger} = 7.7$ kcal.

The simplest of all potentially conjugated organometallic compounds, allyllithium, has been variously described as delocalized, localized, or somewhere in between.[1] It has been subjected to intense theoretical,[2] NMR,[3,4] and crystallographic[5] scrutiny. Allyllithiums exhibit a chameleon-like variety of structures largely determined by the solvation environment and nature of the substituents on allyl.[6-8]

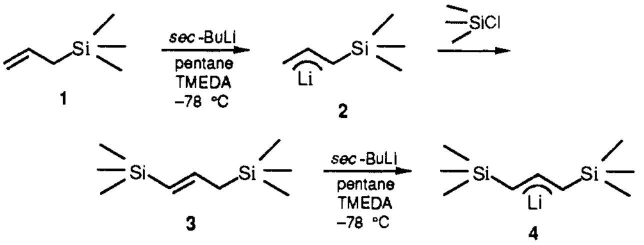
Recently Winchester, Bauer, and Schleyer proposed on the basis of an isotopic perturbation of equilibrium NMR experiment[9] that allyllithium in THF-d_8 is unsymmetrical,[10] a conclusion supported by all published crystallographic studies of simple allyllithiums.[5a-c] In contrast, the isotopic perturbation experiments carried out with allylsodium and allylpotassium showed these two species to be symmetrical.[10] Substituents with conjugating potential appear to favor the delocalized allyllithium structure. For example, (1,3-diphenylallyl)lithium was shown by crystallography to be symmetrical and delocalized.[5d]

Whereas the synthetic utility of (1-silylallyl)lithiums[11,12] is legion, the structures of these interesting compounds remain relatively unknown. That carbanions are stabilized by directly bonded silicon is common knowledge,[13] though how this comes about has been the subject of heated controversy concerning the relative roles of π-carbon overlap to silicon $3p_z$ or 3d orbitals and polarization effects.

To gain some insight into these questions, we have initiated a study of silicon-substituted allyllithiums. This paper deals with the behavior of (1,3-disilylallyl)lithium.[14] Herein we show from NMR studies that in contrast to allyllithium (1,3-disilylallyl)lithium is symmetrical, perhaps due to conjugation of silicons with the allyl moiety, and further that NMR line-shape studies at low temperatures reveal for the first time the rates of rotation of solvated lithium within the tight ion pair.

Results and Discussion

A sample of (3-trimethylsilyl)propene (**1**) was metalated with *sec*-butyllithium at 193 K in TMEDA–pentane and the resulting lithium compound, **2** silylated with chlorotrimethylsilane. Only



one product was detected; it is clearly (*E*)-1,3-bis(trimethylsilyl)propene (**3**), as readily seen from the 1,3 (trans) proton–

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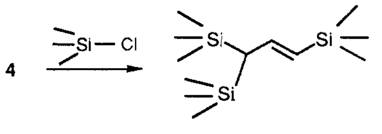
Table I. Proton NMR Shifts (δ, 500 MHz) of [1,3-Bis(trimethylsilyl)allyl]lithium (0.14 M in Diethyl-d_{10} Ether TMEDA, 0.28 M) at Different Temperatures

	145 K	150 K	160 K	180 K	190 K	295 K
$H_{1,3}$	2.60[a]	2.60[a]	2.61	2.59	2.58	2.58
H_2	6.5	6.52	6.50	6.53	6.57	6.57
CH_3Si	−0.05	−0.05	−0.05	−0.05	−0.05	−0.05

[a] Center of gravity; see text.

proton coupling of 18.3 Hz; see Experimental Section for the other proton and ^{13}C NMR parameters. Exclusive silylation at methylene C_3 of **2** closely parallels the results of all electrophile capture experiments with this interesting species.[12]

Metalation of **3** with *sec*-butyllithium in pentane containing 1 equiv of TMEDA produced entirely 1,3-bis(trimethylsilyl)allyllithium (**4**), whose proton NMR spectrum shows it to exist entirely in the exo–exo structure; see below. Finally, silylation of **4** with chlorotrimethylsilane gave exclusively (*E*)-1,3,3-tris(trimethylsilyl)propene (**5**), as indicated by the H_1, H_2 vicinal coupling of 18.2 Hz; see Experimental section for the other proton and ^{13}C NMR parameters.



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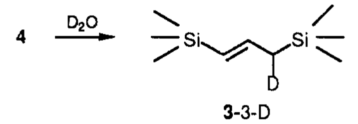
Deuterolysis (D_2O) of disilylallyllithium species **4** afforded 3-3-D, used later in the isotopic perturbation of equilibrium experiment.[9] Proton NMR data ($CDCl_3$ solution) for 3-3-D differs from that of normal **3** only with upfield shifts of C_2H of 0.01 ppm and C_3H of 0.022 ppm. Among the ^{13}C NMR data there are upfield shifts of 0.023 ppm at C_1 and 0.61 ppm at C_3 (HD), due to directly bonded deuterium, compared to **3**.



3-3-D

$$3\text{-}3\text{-}D \xrightarrow[\text{pentane, TMEDA}]{sec\text{-BuLi}} 4\text{-}1\text{-}D + 4$$

Cooling the solution of **4** in pentane–TMEDA to 233 K afforded crystals of composition **4**·TMEDA. After purification (see Experimental Section), the material was dissolved in diethyl-d_{10} ether and in THF-d_8 for subsequent NMR investigation.

In the same general way as described above, **3** was also metalated by *sec*-butyllithium in THF at 293 K and the reaction mixture worked up as before. These samples of **4**, transferred to diethyl-d_{10} ether or THF-d_8, were not studied extensively. They all displayed in their NMR spectra the inimitable signs of competing metalation of THF,[15] the spectrum of its cleavage product lithium acetaldehyde enolate.[16] In fact, for this reason THF should be avoided as a bulk solvent in which to conduct organolithium chemistry.

Proton NMR of a sample of **4**, 0.14 M, in diethyl-d_{10} ether, 0.04 M in TMEDA, exhibits single resonances each for CH_3Si, $H_{1,3}$, and H_2, whose shifts vary hardly at all between 145 and 295 K (see Table I), with one vicinal coupling of 15.5 Hz. Thus, **4** consists of one species in which both trimethylsilyl substituents are exo. This result stands in stark contrast to the widely reported finding that almost all (alkylallyl)lithium compounds exist as mixtures of the exo and endo forms with endo slightly favored at all temperatures investigated.[4a,7,17]

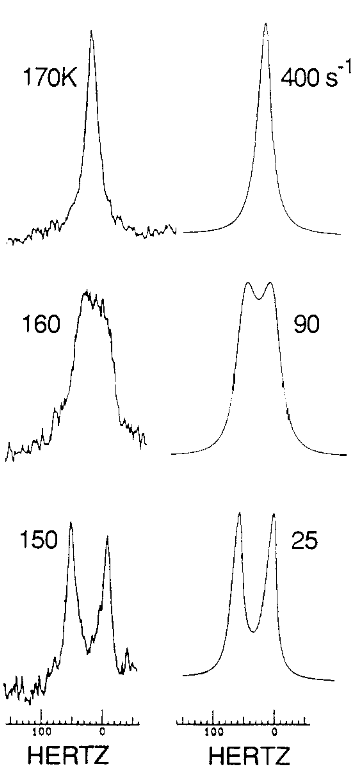


Figure 1. Left: 125-MHz ^{13}C NMR of C_1 and C_3 of **4** (0.14 M with TMEDA, 0.04 M in diethyl-d_{10} ether), at different temperatures (K). Right: calculated line shapes for different rates of site exchange, k_1 s^{-1}.

Carbon-13 NMR of **4** (0.14 M in diethyl-d_{10} ether, 0.14 M in TMEDA, at 140 K) consists of one sharp peak each of CH_3Si and C_2 and an equal doublet, separation 0.48 ppm, for C_1 and C_3 (Figure 1). The appearance of this spectrum and its shifts (including the average shift of C_1 and C_3) changes very little over the entire temperature range used, 140–303 K (see Table II), nor does it depend on the concentration of **4** between 0.14 and 0.55 M. Hence, **4** most likely consists of the same single species over this temperature range. It is possible that some dissymmetry due to solvation of lithium induces the $C_{1,3}$ carbons to be magnetically nonequivalent; see below. However, above 140 K, with increasing temperature there is signal averaging of the $C_{1,3}$ doublet, resulting in a single line at its center by 170 K (Figure 1).

Dynamic effects are also displayed among the ^{13}C resonances for TMEDA in the sample just described. At 140 K, free and complexed TMEDA give rise to clearly resolved spectra (see Figure 2 and Table II), which establish the Li/TMEDA ratio in the complex of **4** to be 1 and show that exchange of TMEDA between its free and complexed states is slow relative to the NMR time scale. Further, the complexed TMEDA gives rise to one ^{13}C line for CH_2 and an equal doublet, separation 4.65 ppm, for the methyl carbons (see Figure 2). With increasing temperature, 160–190 K, this doublet undergoes progressive broadening and signal averaging indicative of some conformational rearrangement within the complex **4**·TMEDA. The latter process is clearly much faster than that which exchanges TMEDA between its free and lithium-complexed states, since by 190 K, the methyl resonance for free TMEDA is still very sharp (see Figure 2). However, by 295 K all free and complexed TMEDA give rise to a single averaged spectrum.

Line shapes for the exchange-dependent C_1/C_3 and NCH_3 ^{13}C resonances of **4** were calculated as two-site uncoupled systems as a function of their respective phenomenological mean lifetimes between successive exchanges.[18] This requires no assumption as to the origin of the process that causes the two kinds of *N*-methyls in the **4**·TMEDA complex to change places. Comparing calculated

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Table II. ^{13}C NMR Shifts (δ, 75 MHz) of **4** (0.14 M in Diethyl-d_{10} Ether, TMEDA, 0.28 M) at Different Temperatures

	140 K	145	160	170	180	190	295
C_1C_3	67.75 (5) 67.25 (4)	67.76 (4) 67.28 (9)	67.65 (1)^a	67.66 (0)^a	67.65 (9)^a	67.70 (4)^a	68.50 (9)^a
C_2	153.10 (2)	153.13	153.25 (6)	153.28	153.49	153.18 (0)	153.94 (0)
NCH_3 (F)^c	46.21 (5)	46.20 (5)	46.18 (6)	46.19 (0)	46.21 (6)	46.20 (5)	
NCH_3 (C)^c	44.44 (4)	44.59 (6)	44.63 (0)	44.61 (0)	45^b		46.97 (1)^a
NCH_3 (C)^c	49.29 (4)	49.11 (8)	49.06 (4)	49.05 (0)	49^b		
NCH_2 (F)^c	58.36 (1)	58.36 (7)	58.40 (5)	58.40 (0)	58.50 (5)	58.55 (0)	
NCH_2 (C)^c	56.68 (6)	56.68 (6)	56.72 (4)	56.73 (0)	56.80 (5)	56.90 (9)	
CH_3Si	1.78 (6)	1.79 (6)	1.76 (5)	1.79 (1)	1.80 (6)	1.81 (0)	2.03 (0)

^{a}Signal averaged. ^{b}Broadened. ^{c}F, free; C, complexed.

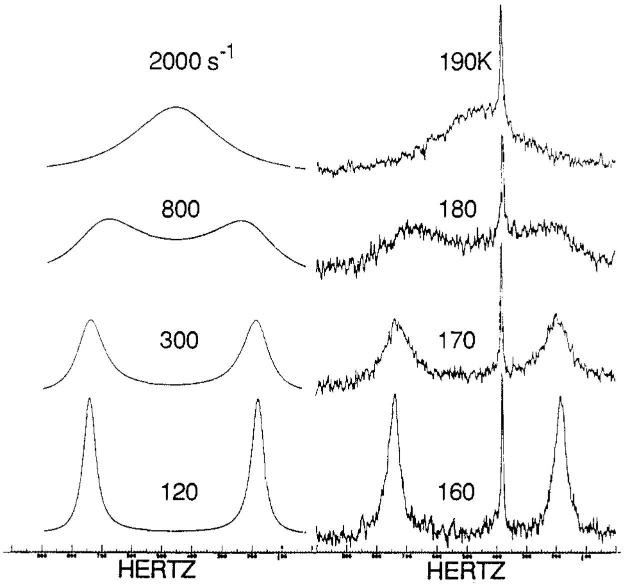


Figure 2. Right: ^{13}C NMR of **4** as described in caption of Figure 1. Methyl resonance of TMEDA at different temperatures (K); sharp truncated resonance is due to free TMEDA. Left: CH_3 line shapes calculated for different rates, k_2 s^{-1}, of site exchange.

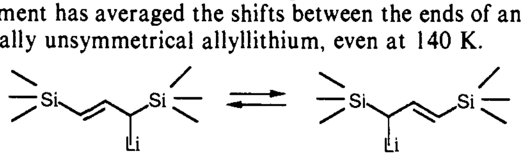
Table III. ^{13}C^a NMR of **4** versus **4**-1-D, TMEDA Complexes (Both 0.08 M in Diethyl-d_{10} Ether) at Different Temperatures

T, K	**4** $\delta(C_{1,3})$	**4**-1-D $\delta(C_3)$	Δ^b
150	67.74 (5) 67.26 (6)	67.63 (5) 67.15 (6)	0.11 0.11
180	67.64 (3)	67.48 (6)	0.16
220	67.84 (6)	67.68 (4)	0.16
303	67.48 (6)	68.34 (0)	0.14

^{a}Referenced to TMS. ^{b}Difference, first column minus second column.

line shapes to the experimental spectra gives rise to the fitted mean lifetimes listed on Figures 1 and 2. Allowing for experimental errors of at most 25%, these τ values obtained from the NCH_3 and C_1, C_3 ^{13}C NMR are so similar that one must assume that the *same process* is responsible for the signal averaging *in both sets* of line shapes, with a $\Delta H^\ddagger$ of 7.7 ± 0.3 kcal. This common mechanism must involve a rearrangement within **4**·TMEDA much faster than the process that exchanges TMEDA between its free and complexed states.

Although the data for **4** favor a symmetrical allylic species with unsymmetrical solvation, it is still possible that some fast rearrangement has averaged the shifts between the ends of an electronically unsymmetrical allyllithium, even at 140 K.



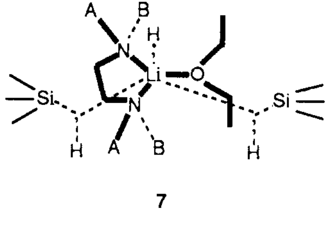
6 **6**

To distinguish between these possibilities, we have carried out a Saunders isotopic perturbation of equilibrium experiment.[9] Thus, a 1:1 mixture of normal **4** and **4**-1-D was prepared from a mixture of the corresponding alkenes, **3** and **3**-3-D, following exactly the method used to prepare the **4**·TMEDA sample.

Carbon-13 NMR of this new preparation, **4** with **4**-1-D, was different from that of **4** alone only in that the C_3 shift in **4**-1-D fluctuates between 0.11 and 0.16 ppm upfield to that of $C_{1,3}$ in **4**, over the entire temperature range used, 140–303 K (see Table III). An equilibrium between two unsymmetrical states would have resulted in temperature-dependent shifts between carbons in **4**-1-D compared to the corresponding ones in reference compound **4**, normal. In fact these shifts are so small and vary so little that species **4** must be regarded as electronically symmetrical with the proviso that some solvation effect renders the C_1 and C_3 carbons magnetically nonequivalent.

Compound **4** was also metalated (*sec*-butyllithium) in THF solution and then the bulk of the THF removed and replaced by THF-d_8 or diethyl-d_{10} ether or toluene-d_8. These samples were all contaminated by lithium acetaldehyde enolate from metalation of THF, as noted above. However, it is interesting that C_1 and C_3 in these samples are always magnetically equivalent, though the shifts are not much different from those in **4**·TMEDA in diethyl-d_{10} ether. Then one would be led to believe that the nonequivalence of C_1 and C_3 in the latter sample might be due to the nature of solvation about lithium.

The result of the deuterium perturbation experiment with **4** and **4**-1-D reported here supports an electronically symmetrical extended conjugated allylic system as was found by X-ray crystallography for (1,3-diphenylallyl)lithium.[5d] Also, X-ray crystallography of a variety of allylic lithium compounds places lithium above the plane of the $C_1C_2C_3$ allyl moiety,[5,19] and in several of these crystals, the ligand coordinated to lithium is dissymmetrically sited with respect to the allyl moiety. Then we would like to propose that **4**·TMEDA contains a planar extended conjugated allyl anion. Normal to the allyl plane above C_2 is lithium coordinated to one TMEDA and to one diethyl ether molecule. The system exists as one conformer in which the coordinated ligands are dissymmetrically sited with respect to the allyl moiety, as has also been observed via X-ray crystallography of other allyllithiums;[5] see **7**. This renders C_1 and C_3 magnetically nonequivalent as well as the two pairs of dimethylamino carbons, as is observed. Structure **7** should give rise to four magnetically nonequivalent N-methyls. The observation of only two is due either to a degeneracy of shifts δ(A) with δ(B) and δ(A′) with δ(B′), see **7**, or to fast inversion at nitrogen, even at 150 K, by individual reversible N–Li bond dissociation. Then the C_1, C_3, and NCH_3 line-shape changes are the result of the rotation of coordinated Li$^+$ with respect to the allyl anionic moiety, the barrier being 7.7 kcal as described above. The same result could be brought about



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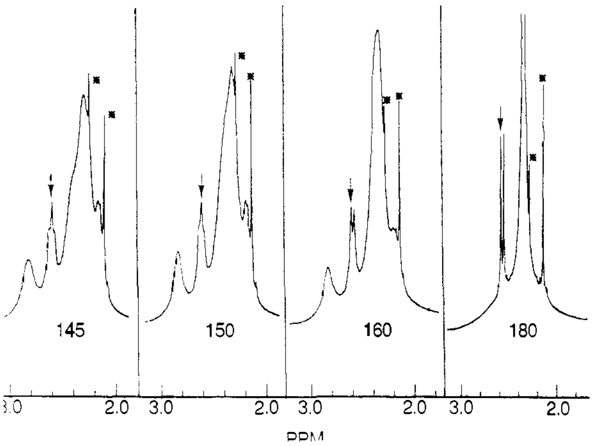

Figure 3. Proton NMR C_1H, C_3H, and TMEDA resonances of sample described in caption to Figure 1 at different temperatures (K); arrows mark C_1H and C_3H absorptions, crosses mark resonance of free TMEDA; see text.

by inversion at Li$^+$, by dissociation of diethyl ether to a transition state in which the plane of the Li$^+$ TMEDA ring bisects that of the anion. This model requires the shift degeneracies $\delta(B) = \delta(B')$ and $\delta(A) = \delta(A')$; see **7**. The choice between rotation of coordinated lithium and inversion at lithium cannot be made unambiguously on the basis of the data presented here. However, in a preliminary study of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine coordinated to (α-trimethylsilylallyl)lithium, it was concluded that line-shape changes in the triamine ^{13}C resonance were due to rotation of coordinated lithium.[20] The only other mechanism that could account for our results is one in which the coordinated lithium undergoes tumbling motions at some distance from allyl. Such a process would also lead to exchange of free with complexed TMEDA, a process shown to be much slower than the internal exchange we attribute to rotation.

Proton NMR of **4** exhibits effects similar to those seen in ^{13}C NMR, though less clearly due to the more limited resolution and to coupling among the methylene protons in complexed TMEDA. Thus, the shifts are largely independent of temperature, except for the C_1H, C_3H doublet (due to vicinal coupling). The latter decoalesces on cooling from 160 to 145 K into a 1:3:1 triplet, i.e., two doublets, with the same intensities, their centers separated by 0.03 ppm (see Figure 3). This reflects the nonequivalence of C_1 with C_3 due to asymmetric solvation of Li$^+$ proposed above.

Interesting upfield deuterium-induced shifts are observed in the proton NMR of **4-1-D** compared to **4** (both TMEDA complexes) of 0.007 ppm for H_3 and 0.0056 ppm for H_2. The remaining proton shifts are the same in both species.

Between 145 and 190 K, proton NMR of **4** (with TMEDA in diethyl-d_{10} ether) shows singlet resonances for free TMEDA at δ 2.12 (CH_3) and 2.28 (CH_2) clearly resolved from the broad ill-defined resonance for complexed TMEDA. On cooling the sample within this temperature range the latter resonance undergoes changes in line shape consistent with slowing rotation of the cooridinated lithium as proposed above (see Figure 3). However, above 190 K, we observe signal averaging of the proton resonances for free and coordinated TMEDA.

In the past, NMR has been an unsuitable technique with which to study structure of ion pairs because most systems investigated underwent very fast exchange of ions among the different ion pairs.[21] More recently, several systems have been uncovered where this ion exchange is slow enough to observe NMR spectra of different ion pairs.[22] In the present example the latter condition also prevails, but in addition, the rotation of one ion (coordinated lithium) with respect to the counterion is slow at 150 K. This has allowed us to determine the structure of the rotamer and the study its dynamics of rotation.

Experimental Section

NMR spectroscopy was carried out with Bruker equipment, AM-500 and MSL 300. Relevant instrumental parameters are as follows:

	^1H	^{13}C
frequency, MHz	500.139	125.76
transform, K	32	32
spectral width, Hz	5000	26315
Hz/point	0.305	1.6
pulse width, μs	8	4
acquisition time, s	3.277	0.62
transients	16	1000

(*E*)-1,3-Bis(trimethylsilyl)propene (3). A 50-mL Schlenk flask containing a magnetic stir bar was dried overnight in an oven, then closed with a septum, evacuated, and finally cooled udner an atmosphere of argon. 3-(Trimethylsilyl)propene (**1**; 5.0 g, 0.044 mol) was introduced together with TMEDA (0.046 mol, 7 mL) and degassed by the freeze–thaw method, followed by 100 mL of THF (freshly distilled from Na–K benzophenone). After the flask was cooled to −78 °C, a solution of *sec*-butyllithium in pentane (34 mL, 1.3 M, 0.0442 mol) was added dropwise via syringe over 15 min. The reaction mixture was allowed to warm to room temperature over 1 h and then cooled again to −78 °C. Trimethylchlorosilane (5.0 g, 4.3 mL, 0.109 mol) was added dropwise over 10 min. Hydrolysis with excess water at room temperature followed by ether extraction and drying the ether extracts with magnesium sulfate yielded, after removal of solvent and vacuum distillations of the residue, 3.6 g of the title compound: 44% yield; bp 75–77 °C (28 Torr); proton NMR (500 MHz) δ 5.545 (C_1H), 6.018 (C_2H), 1.663 (C_3H_2), 0.04 and 0.05 ($SiCH_3$); *J*, Hz, C_1H, C_2H 18.3, C_1H, C_3H_2 1.04, C_2H, C_3H_2 7.8, C_3H, C_3D 1.53; ^{13}C NMR (125 MHz) δ 128.08 (C_1), 143.66 (C_2), 28.38 (C_3), −1.01 (4) and −2.11 (5) (CH_3Si).

[1,3-Bis(trimethylsilyl)allyl]lithium (4·TMEDA) Complex. *sec*-Butyllithium in pentane (4 mL, 1.3 M, 5.2 mmol) was slowly added by syringe to a solution of 1 mL of TMEDA in 10 mL of pentane cooled to −78 °C. After the precipitate that formed was warmed to room temperature the resulting solution was allowed to react slowly with 1,3-bis(trimethylsilyl)propene (1 g, 5.3 mmol). At this point evolution of gas was observed. When this solution was cooled to −40 °C a yellow precipitate formed, which was cold filtered at this temperature. Then volatile components (pentane and excess TMEDA) were removed under reduced pressure (0.1 Torr). A sample of the resulting crystals was dissolved in diethyl-d_{10} ether (420 mg) for NMR investigation. This solution was 0.14 M in **4**·TMEDA and pentane could not be detected by NMR. Samples of **4**·TMEDA were also dissolved in THF-d_8.

(*E*)-1,3-Bis(trimethylsilyl)propene-*3*-*d* (3-3-D) and (*E*)-1,3-Bis(trimethylsilyl)propene (3). In similar fashion to the above preparation of **3**, 3-(trimethylsilyl)propene (4.3 g, 6 mL, 38 mmol) was reacted with *sec*-butyllithium in pentane (30 mL, 1.3 M, 39 mmol) in 50 mL of THF at −78 °C under argon. On completion of the metalation this solution was cooled to −78 °C and reacted with chlorotrimethylsilane (4.1 g, 39 mmol). After warming the reaction mixture to room temperature over 1 h to ensure complete silylation and recooling to −78 °C *sec*-butyllithium (30 mL, 1.3 M, 39 mmol) was slowly syringed in and the system rewarmed to room temperature. Finally, 15 mL of D_2O (excess) was slowly introduced by syringe. Workup as described above gave 4.6 g of a mixture of the all proton and monodeuterio title compounds, in ratio 1:1, in 65% yield based on starting **1**, bp 80 °C (32 Torr).

[1,3-Bis(trimethylsilyl)allyl]lithium-*1*-*d* (4-1-D·TMEDA) and [1,3-Bis(trimethylsilyl)allyl]lithium (4·TMEDA). The title compounds were prepared via *sec*-butyllithium metalation of the alkene mixture **3** and **3-3-D**, exactly as described above for the metalation of **3** alone.

[1,3-Bis(trimethylsilyl)allyl]lithium (4) Prepared in THF. Disilylpropene **3** (0.37 g, 2 mmol) in 20 mL of THF was degassed by the freeze–thaw method. Under an atmosphere of argon this solution was cooled to −78 °C and then treated dropwise over a period of 15 min with *sec*-butyllithium (1.3 mL, 1.3 M, 1.95 mmol). After the reactive mixture was allowed to warm to room temperature (1 h), all volatile components were removed in vacuo. The resulting powder was dissolved in toluene-d_8–diethyl-d_{10} ether and in THF-d_8 for NMR examination.

4·PMDTA. Alkene **3** (0.280 g, 1.34 mmol) in 20 mL of diethyl ether containing *N,N,N′,N′,N″*-pentamethyldiethylenediamine (PMDTA; 2.32

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g, 1.34 mmol) was treated with a pentane solution of *n*-butyllithium (1.1 mL, 1.3 M, 1.45 mmol) (15 min) at −78 °C under an atmosphere of argon. After the reaction mixture was warmed to room temperature over the course of an hour, all volatile components were removed in vacuo. A red-black solid remained, which was dissolved in toluene-d_8 for NMR examination.

(*E*)-**1,3,3-Tris(trimethylsilyl)propene (5).** Under an argon atmosphere at −78 °C (dry ice–2-propanol) *sec*-butyllithium (66 mL, 1.3 M, 95.8 mmol) in pentane was slowly syringed into a stirred solution of (*E*)-1,3-bis(trimethylsilyl)propene (**3**; 16 g, 86 mmole) in 50 mL of THF. The mixture immediately turned red. After stirring for 1 h, the resulting solution was allowed to warm to room temperature and then reacted with trimethylsilyl chloride (9.4 g, 11 mL, 86 mmol). Hydrolysis, extraction into diethyl ether, and removal of the ether yielded, after vacuum distillation of the residue, 10.9 g of the title compound: 49% yield; bp 116–120 °C (31 Torr); proton NMR (CDCl$_3$) δ 5.32 (C_1H), 5.87 (C_2H), 1.18 (C_3H), 0.84 and 0.52 (CH_3Si), (1:2); *J*(X,Y), Hz, C_1H, C_2H 18.2, C_1H, C_3H 0.4, C_2H, C_3H 11.4; ^{13}C NMR δ 127.59 (C_1), 145.22 (C_2), 31.53 (C_3), −0.92 and −0.56 (TMS) (1:2).

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Influence of Molecular Correlation Time on the Homonuclear Overhauser Effect in Paramagnetic Proteins

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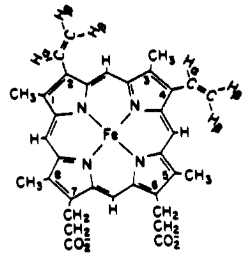
Abstract: The effect of solvent viscosity on the nuclear Overhauser effect, NOE, in paramagnetic myoglobin complexes has been investigated to determine the influence of the overall molecular correlation time on the magnitude of NOEs. We show that steady-state NOEs in these paramagnetic complexes are strongly decreased relative to isostructural diamagnetic systems but that this dramatic diminution characteristic of NOEs in paramagnetic complexes can be moderated by selectively increasing cross-relaxation, provided the electron spin–lattice relaxation time, which dominates intrinsic nuclear relaxation, is independent of the overall molecular motion of the complex. In such cases, the steady-state NOE will increase with the overall correlation time, τ_c, asymptotically approaching that NOE characteristic of an isostructural diamagnetic system. Steady-state NOE experiments on strongly paramagnetically relaxed and hyperfine-shifted resonances in high-spin ferric–aquo and low-spin ferric–cyano complexes of sperm whale myoglobin demonstrate that the NOE doubles upon doubling the viscosity by adding 30% ethylene glycol. The cross-relaxation rates determined via a truncated NOE experiment double, as expected with doubling the viscosity, and the increased steady-state NOE hence indicates that the iron T_{1e} is independent of τ_c. Such an independence of T_{1e} on τ_c in hemes in general is demonstrated for the model compound dicyano[tetrakis(4-sulfophenyl)porphine]iron(III) for which T_{1H} (and hence T_{1e}) is found unchanged when the solvent viscosity is varied 40-fold in mixtures of water and glycerol. The increased NOEs with τ_c provide a rationalization for earlier observations of vastly increased NOEs for model complexes in viscous solvents and improved NOE data in large hemoprotein systems and suggest that not only should NOEs be profitably pursued for a variety of paramagnetic proteins but such studies (in contrast to diamagnetic proteins in the slow-motion limit) may more likely be successful in larger rather than smaller proteins.

The importance of the nuclear Overhauser effect, NOE, in modern structural studies of biopolymers by NMR, either in the one-dimensional variation or in the form of the two-dimensional NOESY map, is underscored not only by its critical role in resonance assignments but also by its ability to provide the unique nonbonded constraints that form the basis of complete structure determination of small diamagnetic biopolymers ($M_r \leq 15 \times 10^3$) in solution.[1-3] The efficacy of the NOE depends on the ^{1}H–^{1}H dipolar interaction as the dominant proton relaxation mechanism.[4] Hence, the dominance of electron–nuclear dipolar relaxation of protons in paramagnetic molecules[5,6] was initially thought to render NOEs undetectable. This dominant paramagnetic relaxation mechanism is clearly observed for the hyperfine-shifted resonances of all paramagnetic molecules[5-7] and, in particular, for the class of heme proteins that possess the iron protoporphyrin group **1** capable of existing in no less than seven relatively stable paramagnetic states for the three common oxidation states.[8,9] However, in spite of the strong dominance of paramagnetic relaxation influences in all protein forms studied to date, it has been possible to obtain useful ordinary steady-state or time-dependent NOE data for a variety of hemoproteins.[10-13] In two cases, highly informative two-dimensional NOESY maps have been obtained



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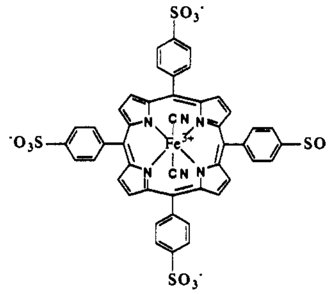

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