$$V_3(\theta) = \frac{V_3}{2}(1 - \cos 3\theta) + \frac{V_6}{2}(1 - \cos 6\theta) + \ldots$$

A potential function of this type is shown in the last line of Figure 21.

It is reasonable to suppose that the barriers to rearrangement *can* be much higher for the XML_4 complex than for the ML_5 since in the former case twofold terms in the potential function may be nonzero for cycle A and threefold terms may be nonzero for cycle B. In general, highly periodic barriers are observed to be low, and this idea has been found to be useful in consideration of barriers to internal rotation and barriers to pseudorotation in small cyclic systems.

In the case of an XML_4 complex with X equatorial and with C_{2v} symmetry, the barriers have the same form as those shown in rows 2 and 3 of Figure 21; consequently, the barrier can be high. However, in the case of path A with the minima at $\pi/3$, $2\pi/3$, $4\pi/3$, and $5\pi/3$ (corresponding to X in an axial position) now lower than those at 0, π, and 2π (X equatorial), the chemical shifts and coupling constants can be averaged by a Berry-type process which exchanges the molecule between the equilibrium configurations at approximately $\pi/3$ and $2\pi/3$ and between those at approximately $4\pi/3$ and $5\pi/3$ with X as the pivotal ligand. Consequently the full barrier need not be overcome and since θ changes by only about $\pi/3$ in the exchange process the effective barrier should be low. This seems to be the case with the exception of systems in which the X–M bond has partial double bond character.[2,32,33] In the case of an X_2ML_3 system with the two X ligands equatorial (C_{2v} symmetry) θ must change by $\sim 2\pi/3$, at least, in order to reach another equivalent potential energy minimum and a large barrier can be anticipated. The above discussion was confined to complexes undergoing a Berry type of motion. However, because of the large number of equivalent energy minima for ML_5 systems, the barrier to rearrangement is expected to have a higher periodicity and consequently *may* have a smaller magnitude than for similar X_nML_{5-n} systems in cases where the rearrangement mechanism is different.

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Hindered Rotation in Trimethylsilyl Amides

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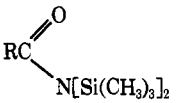
Abstract: Rotational barriers were determined for *N-tert*-butylformamide (I) and *N*-trimethylsilylformamide (II) in chlorobenzene by the total line-shape procedure. Barriers for *N*-methyl-*N*-trimethylsilylformamide and -acetamide were obtained by an approximate method. The free energy of activation for II extrapolated to infinite dilution is 3 kcal/mol lower than that for I. A rationalization based on the (p–d)π model is offered. Isomer ratios were measured for all compounds. Activation parameters for bis(trimethylsilyl)acetamide were also determined by the total line-shape procedure and compared with those of the mono derivatives.

While the effect of third period atoms on inversion processes at nitrogen and phosphorus has recently been investigated,[1] their effect on the rotational process in the classical amide system has received little attention. We present here the results of an investigation of the rotational barriers in a series of trimethylsilyl amides. These compounds, some of which have been used extensively as silylating agents,[2] are also interesting from a structural standpoint. The monotrimethylsilyl amides, such as *N*-methyl-*N*-trimethylsilylacetamide, are generally conceded to have the silyl group attached to nitrogen.[2b] The bis derivatives, on the other hand, have been reported as *N,N*-bis(trimethylsilyl)-substituted amides (**1**)[2b] and as *N,O*-bis(trimethylsilyl)-substituted imidates (**2**).[3] Both types



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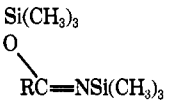

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of compounds, mono and bis substituted, exhibit temperature dependent nmr spectra which could be ascribed to either hindered rotation about the C–N bond or exchange of trimethylsilyl groups.

The present work, then, is an attempt to (a) determine the effect of *N*-trimethylsilyl substitution on the rotational barrier in amides and (b) lay the groundwork for a more rigorous examination of the structure of bis(silyl) amides and related compounds.

Experimental Section

Compounds. Bis(trimethylsilyl)acetamide was obtained from the reaction of trimethylchlorosilane with acetamide according to the procedure of Klebe, *et al.*,[4] bp 50° (11 mm) [lit.[4] 71–73° (35 mm)]. Trimethylsilylacetamide was prepared from the reaction of equi-

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molar amounts of trimethylchlorosilane, acetamide, and triethylamine in benzene, bp 75° (10 mm) [lit.[4] 105–107° (35 mm)]. *N*-Methyl-*N*-trimethylsilylacetamide was prepared from trimethylchlorosilane and *N*-methylacetamide in excess triethylamine, bp 154° [lit.[5] 154° (770 mm)]. *N*-Methyl-*N*-trimethylsilylformamide was obtained by refluxing equimolar amounts of *N*-methylformamide, trimethylchlorosilane, and triethylamine in benzene, bp 78–79° (12 mm) [lit.[6] 75° (20 mm)]. Trimethylsilylformamide was prepared *via* transamination of trimethylsilyl-*tert*-butylamine with formamide according to the procedure of Horwitz and deBenneville,[7] bp 93° (28 mm) [lit.[7] 84–85° (21 mm)]. *N*-*tert*-Butylformamide was obtained by the procedure of Ritter and Kalish,[8] bp 81–82° (8 mm) (lit.[9] 200–202°).

Spectra. Nmr spectra used for the determination of activation parameters were obtained on a Varian A-60D spectrometer equipped with variable temperature accessory V-4341/V-6057. At least three traces of the area of interest, *i.e.*, the $Si(CH_3)_3$ or $C(CH_3)_3$ region, were run at 50-Hz sweep width and 500-sec sweep time. Peak locations in the $Si(CH_3)_3$, $C(CH_3)_3$, and NCH_3 regions were determined by the standard side banding method using a Hewlett-Packard 200CD audio oscillator and Model 522B electronic counter. Temperatures were measured with the standard methanol and ethylene glycol samples and the equations of Van Geet.[10]

Chlorobenzene was used as solvent and dried over molecular sieves (Linde type 4A).

Determination of Rates and Activation Parameters. Activation parameters for the bis derivative were determined with the total line-shape procedure described previously.[11] The limiting separation, $\Delta\nu_0$, was found to have very little dependence on temperature below the coalescence temperature and was taken as 8.08 Hz; T_2 was determined from the half-height width of internal TMS.

Rate constants for *N*-*tert*-butylformamide and *N*-trimethylsilylformamide were determined as follows. The Gutowsky–Holm equation modified[12] to include two transverse relaxation times was programmed in Fortran IV. The computer output was interfaced (TSP-12) to a Honeywell Model 530 *x*–*y* plotter.

Populations were determined at five or six temperatures below the coalescence region by weighing the peaks cut from good grade paper. The populations at each temperature are averages determined from at least three tracings. A least-squares analysis of $\log P_b/P_a$ *vs.* $1/T$ was then used to evaluate P_a and P_b at any desired temperature. The limiting separation, $\Delta\nu_0$, was also determined at four or five temperatures in the "slow exchange" region. The least-squares plot of $\Delta\nu_0$ *vs.* T was used to obtain $\Delta\nu_0$ at any temperature.

An approximate value of T_2 for each peak was obtained from its half-height width at a low temperature. These T_2 values were then modified as follows. For two temperatures, one near the region of maximum $\Delta\nu_0$ and the other near coalescence, the T_2 values and τ were varied (population and $\Delta\nu_0$ as determined above were the other input) until the computer-generated curve matched (*vide infra*) the experimental curve. The shape of the curve was found to be quite sensitive to the magnitude of the difference between the two T_2 values, especially in the near coalescence region. A plot of the two sets of T_2 values *vs.* T was then used to determine the T_2 values at any temperature.

With the extrapolated populations, $\Delta\nu_0$, T_{2a}, and T_{2b} values as constants, the computer-generated spectrum was fitted to the experimental spectrum at a particular temperature by varying τ until the visual match of the two spectra was as good as possible (weighting heavily the match in relative peak heights, the height of the minimum, the width of the larger peak, and the separation of the two peaks).

Rate constants were determined from τ at a given temperature from the relations $k_a = P_b/\tau$, $k_b = P_a/\tau$. Activation energies were determined from Arrhenius plots of $\log k$ *vs.* $1/T$. The free energies of activation were determined at 25° from the Erying equation, assuming a transmission coefficient of unity.

The use of τ values, which produced the next-to-best fit of computer spectrum to experimental spectrum, resulted in an estimate of the error in E_a of $\pm$ 0.8 kcal, but only $\pm$0.3 kcal for $\Delta G^{\ddagger}$.

The free energies of activation for *N*-methyl-*N*-trimethylsilylformamide and -acetamide at their coalescence temperatures were calculated by the method of Shanan-Atidi and Bar-Eli[13] using extrapolated $\Delta\nu_0$'s and populations for the trimethylsilyl peaks. The calculations were checked with data based on the *N*-methyl peaks.

Results and Discussion

Structure. The nmr spectra of the mono derivatives, except *N*-trimethylsilylacetamide, contain two peaks of unequal area in the trimethylsilyl region below a certain temperature. As the temperature of these derivatives is increased, the shape of the peaks follows the usual coalescence pattern. The behavior of the peaks in the remainder of the spectrum of each derivative is also consistent with the removal, or averaging, of magnetic nonequivalence as a function of temperature. Chemical shifts of $M(CH_3)_3$ (M = C or Si) and $N-CH_3$ groups in the slow exchange region are given in Table I.

The structures of the rotamers responsible for each nmr signal were assigned by making use of (a) the fact that dilution with aromatic solvents, in this case chlorobenzene, results in a greater upfield shift for the isomer with the *N*-alkyl group trans to carbonyl, and (b) that CH_3CONCH_3 and $HCONCH_3$ trans proton–proton coupling constants are greater than cis coupling constants.[14] The more intense $N-CH_3$ peak in the spectrum of *N*-methyl-*N*-trimethylsilylformamide is a doublet, whereas the less intense peak is a broad singlet; the intense peak can therefore be assigned to the $N-CH_3$ group in the isomer with CH_3 cis to the carbonyl. Likewise, in the spectrum of *N*-methyl-*N*-trimethylsilylacetamide, the less intense $N-CH_3$ peak is broader than the more intense peak; the most abundant isomer, therefore, has $Si(CH_3)_3$ cis to the carbonyl. All assignments were confirmed by the dilution criterion. The structural formulas given in Table I represent the structure of the most abundant isomer for each compound. These structures are in complete agreement with the isomer trends observed previously for mono- and disubstituted formamides and acetamides.[14]

Table I also contains the isomer populations in the slow exchange region. The value for *N*-trimethylsilylformamide is identical, within experimental error, with that of the carbon analog. At first glance this similarity may be surprising since the covalent radius of silicon is larger than that of carbon, and for *N*-alkylformamides the percentage of the isomer with the alkyl group cis to carbonyl is believed to decrease as the size of the alkyl group increases.[15] A careful examination of space-filling models of the Stuart–Briegleb type reveals, however, that the spatial demand (hindrance) of the trimethylsilyl group is quite comparable with that of the *tert*-butyl group in these amides. Of course, other factors, such as nonbonded interactions and differences in electronic structure, may also affect the isomer ratio.

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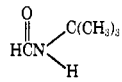
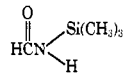
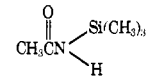
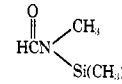
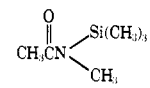
Table I. Chemical Shifts and Isomer Ratios

		Chemical shifts, Hz[a]						
		$M(CH_3)_3$		$N-CH_3$		T, °C[b]	% abundance[c]	T_c, °C[d]
		Major	Minor	Major	Minor			
I		81.1	69.1			−20	72	89
II		14.7	7.2			−20	73	49
III		15.0					100	
IV		7.2	13.4	158.7 (d)	155.2	20	87	71
V		14.9	6.1	148.8	163.3	−40	93	−3
VI	$CH_3CON[Si(CH_3)_2]_2$	7.6	15.7			−30		11

[a] Chemical shift for 30% v/v solutions in C_6H_5Cl downfield from TMS at 60 MHz. [b] Slow-exchange region in which shifts and populations were measured. [c] Abundance of isomer represented by structural formulas at left. [d] Temperature at which $Si(CH_3)_3$ peaks coalesce.

Only one peak in the $Si(CH_3)_3$ region was observed for *N*-trimethylsilylacetamide down to −40°. This could be attributed to (a) the presence of only one isomer, (b) the same chemical shifts for the $Si(CH_3)_3$ groups of both isomers, or (c) a low barrier to rotation about the carbonyl–nitrogen bond. Because of the magnitude of the rotational barrier in *N*-trimethylsilylformamide (the acetamide barrier would be slightly lower) as discussed below and the observation of only one peak in *N*-*tert*-butylacetamide,[15] the best explanation appears to be a. The greater abundance of the cis (alkyl cis to oxygen) isomer of the acetamide relative to the formamide is reasonable in light of the similar observation of LaPlanche and Rogers.[15]

Activation Parameters. Table II lists the activation parameters for compounds I, II, and VI as determined by the total line-shape method. The free energies of activation for compounds IV and V were obtained by the method of Shanan-Atidi and Bar-Eli (*vide supra*).[13] For the unsymmetrical amides, two sets of parameters are given: one set for the conversion of the least abundant isomer A to the more abundant isomer B (A → B) and the other set for the reverse process (B → A). Because of the probable effect of intermolecular association on the rotational barriers of I and II, these parameters were determined at two concentrations in the 5–30% region and extrapolated to infinite dilution.

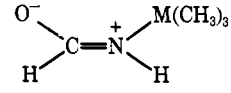
Table II. Activation Parameters

Compound	E_a, kcal/mol		Log A		$\Delta G^{\ddagger}$, kcal/mol[a]	
	A → B	B → A	A → B	B → A	A → B	B → A
I (30%)	22.6	23.8	14.9	15.3	19.8	20.4
(infinite dilution)					19.0	19.3
II (30%)	19.8	20.8	14.5	14.7	17.5	18.15
(infinite dilution)					16.1	16.5
IV (30%)					18.5	19.8
V (30%)					14.4	15.8
VI (30%)	12.2		10.5		15.3 (15.5)[b]	

[a] Calculated at 298°K, except for IV and V which are calculated at T_c. [b] Value in parentheses obtained when intensity ratio method[12] was used.

As is evident from Table II, the parameters for I and II are indeed solvent dependent and probably are not a completely accurate reflection of the rotational process. Hopefully, however, a comparison of the parameters for I and II at a given concentration, especially infinite dilution, can provide a comparison of the rotational barriers in these derivatives. Since free energies of activation are known to be considerably less sensitive to experimental error than energies of activation, the comparisons below will be based on this parameter. For I and II the energies of activation parallel the free energies.

Comparison of either the 30% or infinite dilution $\Delta G^{\ddagger}$ values for I and II shows that the values for II are 2–3 kcal/mol lower than those of I. Since the steric requirements of the *tert*-butyl and trimethylsilyl groups are quite similar (*vide supra*), the difference can be attributed to electronic effects. Although little is known about the electronic effects of the N substituent on rotational barriers, it would appear that the lower electronegativity and greater polarizability of silicon relative to carbon should result in a greater contribution of resonance structure **3** when M = Si. This, in turn,



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should produce a decrease in the ground state energy of the molecule and raise the rotational activation energy relative to the M = C analog. The experimentally observed decrease in the activation energy can be attributed to the often-invoked (p–d)π interactions between

nitrogen and silicon which are unlikely when M = C. These interactions should (a) reduce (p–p)π overlap between carbon and nitrogen in structure **3** and thereby increase the energy of the ground state and (b) lower the energy of the transition state (where the (p–d)π overlap should be greater). The combination of these consequences should result in a lower activation energy for *N*-trimethylsilylformamide.

The average values of $\Delta G^{\ddagger}$ for IV and V are 2–3 kcal lower than recent values for dimethylformamide (21.0 kcal/mol)[16] and dimethylacetamide (18.1 kcal/mol),[17] respectively. Substitution of a trimethylsilyl group for a methyl group produces, therefore, a decrease of 2–3 kcal in the free energy of activation. This decrease is probably attributable to (a) the greater size of the trimethylsilyl group relative to a methyl group which would result in destabilization of the ground state and a consequent lowering of the rotational barrier[14,18] and (b) (p–d)π interactions as discussed above.

If the structure of compound VI is that given by representation **1**, the rotational barrier would be expected to be somewhat lower than the barrier in V because of the steric and electronic effects wrought by substitution of the *N*-methyl group in V by the trimethylsilyl group. The magnitude of the decrease would almost certainly not be as large as the difference between dimethylformamide and V, however, due to competitive (p–d)π interactions between the nitrogen and both silicons of VI. Thus, the barrier in VI could be predicted as, say, 1–3 kcal/mol lower than that of V. The barrier in VI as judged by $\Delta G^{\ddagger}$ is, in fact, the same as that of V, and consequently no assignment of structure is possible. Only if the experimental barrier were grossly different from the predicted barrier, could even a tentative assignment be made. Clearly, further work on the structure of the bis derivative is necessary.

Acknowledgments. The authors are indebted to the Du Pont Co. and the Camille and Henry Dreyfus Foundation for partial support of this work.

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Acidity of Hydrocarbons. XLII. Effect of Temperature on the Absorption Spectra of Some Lithium and Cesium Salts of Carbanions in Amine Solvents[1]

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Abstract: Fluorenylcesium, indenylcesium, and triphenylmethylcesium in cyclohexylamine (CHA) or in CHA–diethylamine show little effect of temperature on the visible absorption spectra, indicating that these compounds exist primarily as contact ion pairs in these solutions. The spectra of fluorenyllithium and indenyllithium in CHA–Et_2NH are temperature dependent and indicate an equilibrium between contact and solvent-separated ion pairs; these compounds are 95 and 65%, respectively, solvent-separated ion pairs at room temperature. Triphenylmethyllithium has a strongly temperature-dependent spectrum in CHA; deeply colored solutions at room temperature are colorless above 100°. The results are interpreted in terms of an equilibrium between solvent-separated ion pairs and the hydrocarbon; that is, the relative acidity of the hydrocarbon depends on the specific anion or ion-pair nature of its conjugate base. A simple electrostatic treatment is shown to account satisfactorily for the difference between contact ion pair acidity and solvent-separated ion pair acidity for several hydrocarbons with planar anions.

The dual concept of contact and solvent-separated ion pairs in organic chemistry[2] was first extended to carbanion systems by Hogen-Esch and Smid[3] with their important analysis of spectra as a function of temperature. We report the application of their analysis to the effect of temperature on the absorption spectra of some lithium and cesium salts of carbanions in solvents containing cyclohexylamine (CHA). The present study has especial significance because of the large and growing number of quantitative relative acidities determined by our research group for lithium and cesium salts of hydrocarbons in the cyclohexylamine solvent.[4]

The effect of temperature on the absorption spectrum of fluorenyllithium in cyclohexylamine–diethylamine (2:1 molar ratio) is shown in Table I. The use of the mixed solvent allowed measurements at lower temperatures than with CHA alone. The positions of the absorption maxima at 452, 480, and 512 nm and the peak ratio at low temperature resemble closely those

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