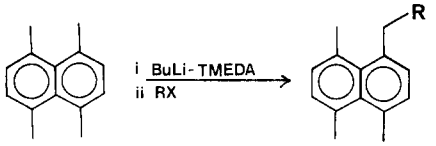
As a consequence of these results, we wonder if perhaps the anion of **9**, which Hart[2] has reported to give the benzylic products **10** and **11** on quenching with $(CH_3)_3SiCl$ and CH_3I, respectively, is also ambident. Our calculations (Table II) suggest that it might be, and because of the severe steric effect in 1,8-naphthalenes,[15] we would anticipate again that ring substitution would be preferred for trimethylsilyl chloride. As with **6**, assignment of the product identity by spectroscopic means is liable to error.



9

10 R = $SiMe_3$
11 R = Me

Similar calculations with the anions of 1-methyl- and 1,4-dimethylnaphthalene (see Table II) suggest that substitution on the ring adjacent to the benzylic group is a possibility, though perhaps not as likely as for **1**. We have also calculated the results expected for 1,2,3,4-tetramethyl- and 1,2,3,4,5,8-hexamethylnaphthalene, and these calculations agree with the experimental results found by Hart.[2] While synthetically we have made no attempt to examine the scope of this effect, we hope that this note will caution others to take cognizance of it in their investigations.

Experimental Section

^1H NMR spectra were determined in $CDCl_3$ on a Perkin-Elmer R32 (90 MHz) spectrometer (Me_4Si as internal standard). GC–mass spectra were recorded on a Finnigan 3300 mass spectrometer using methane chemical ionization. Relative intensities are reported in parentheses.

General Procedure. *n*-Butyllithium (5 mmol in hexane (3.4 mL)) was added to TMEDA (0.8 mL, 5 mmol) in a flame-dried flask, under N_2 at 0 °C with stirring. After 15 min a solution of 2,3-dimethylnaphthalene (156 mg, 1 mmol) in THF (5 mL, distilled from $LiAlH_4$) was added. The mixture was kept at 0 °C for a further 15 min and then was allowed to warm to ~20 °C and stirred for 24 h. The appropriate electrophile ($(CH_3)_3SiCl$, Br_2, CH_3I, or D_2O; 5.5 mmol) was then added, and the resulting mixture was stirred again for 24 h. Water and CH_2Cl_2 were then added, and the organic extract was dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel with pentane as eluant. Product purity and identity were established by ^1H NMR and GC–mass spectrometry.

No attempts have been made to optimize yields, but in all cases some **1** is returned, and this is not reduced by longer reaction times; it is possibly formed by **3** acting as a base with some of the electrophiles or solvent or on workup.

2-(Deuteriomethyl)-3-methylnaphthalene (4): an oil in about 80% yield; ^1H NMR δ 7.75–7.55 (m, 2, H-5,8) 7.50 (s, 2, H-1,4), 7.45–7.25 (m, 2, H-6,7), 2.30 (br s, ~5, CH_2D, CH_3; this peak was broadened due to D coupling); GC–MS (CI), *m/e* 186 (M + 29, 15), 185 (<5), 158 (M + 1, 95), 157 (M, 100) 156 (M - 1,32). Anal. Calcd for $C_{12}H_{11}D$: C, 91.67; H + D, 8.33. Found C, 91.33; H + D, 8.30.

2-Ethyl-3-methylnaphthalene (5): an oil in about 75% yield; ^1H NMR δ 7.85–7.65 (m, 2, H-5,8), 7.58 (s, 2, H-1,4), 7.45–7.25 (m, 2, H-6,7), 2.75 (q, J = 7.5 Hz, 2, CH_2CH_3), 2.42 (s, 3, Ar CH_3), 1.30 (t, J = 7.5 Hz, 3, CH_2CH_3); GC–MS (CI), *m/e* 199 (M + 29,8), 171 (M + 1, 100), 170 (M, 90) 169 (M - 1,14), 155 (M - 15,31). Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.65; H, 8.17.

2,3-Dimethyl-1-(trimethylsilyl)naphthalene (6): an oil in about 70% yield; ^1H NMR δ 7.85–7.25 (m, 5, Ar H) 2.41 and 2.29 (s, ~3 each, Ar CH_3), 0.05 (s, 9, $Si(CH_3)_3$); GC–MS (CI), *m/e* 257 (M + 29, 4), 229 (M + 1, 42), 228 (M, 48), 73 ($Si(CH_3)_3^+$, 100). Anal. Calcd for $C_{15}H_{20}Si$: C, 78.88; H, 8.83. Found: C, 79.20; H, 8.69.

Reaction of this compound at ~20 °C with 1:1 methanol–H_2SO_4 returned 2,3-dimethylnaphthalene (**1**) in essentially quantitative yield.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support of this work.

Registry No. **1**, 581-40-8; **3**, 84498-93-1; **4**, 84498-94-2; **5**, 31032-94-7; **6**, 84498-95-3.

Supplementary Material Available: Molecular orbital calculations for all atoms (4 pages). Ordering information is given on any current masthead page.

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Transition-State Pliability in N-to-N Proton Transfer

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Received November 16, 1982

Partial atomic charges and bond orders in transition states are commonly estimated from isotope effects and Brönsted coefficients. Transition states with, for example, "0.20 partial atomic charge" or "0.37 fraction of reaction progress" abound in the literature.[1,2] Importantly, and this is seldom stated explicitly, a partial charge or bond order in a transition state almost certainly represents a weighted average derived from an *array* of transition-state geometries. In this respect partial bonds resemble intermolecular hydrogen bonds where greater than half the population can deviate by 20° or more from linearity.[3] Since chemists have, however, little notion as to the pliability of transition states, they are unable to assign significance to numbers such as "62% bond breakage". Does this value mean that most transition-state contributors fall within the 62 ± 5% range? Or is the distribution curve broad so that a substantial number of contributors possess greater than 72% or less than 52% bond breakage? One would like to know, in short, the width of the potential valley in which the transition state lies.

We have attacked the problem of transition-state pliability both experimentally and theoretically. In the experimental approach, we synthesized rigid hydroxy acids for which the lactonization trajectories differ while other parameters (OH/C=O distances and ring strain in the lactones) remain constant.[4] It was found that within the confines of a 10° angle variation, lactonization rates are invariant. In the present paper, we utilize the MINDO/3 method to secure energies[5] for N-to-N proton transfer in $NH_2CH_2NH_3^+$. Calculations, employing a Davidon–Fletcher–Powell optimization subroutine, were used initially to locate the minimum position of the mobile proton

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(5) Semiempirical methods such as MINDO/3 have limitations, some of which are discussed in M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977). These limitations are not so important in our calculations because we are concerned with *changes* in energy rather than with *absolute* energy values.

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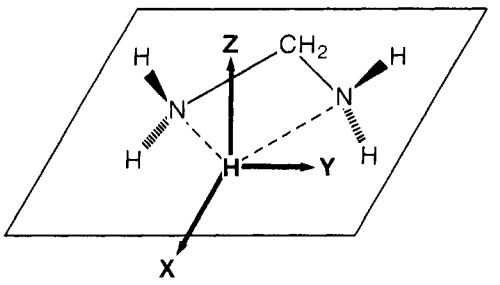

Figure 1. Transition state for N-to-N proton transfer in $NH_2CH_2NH_3^+$.

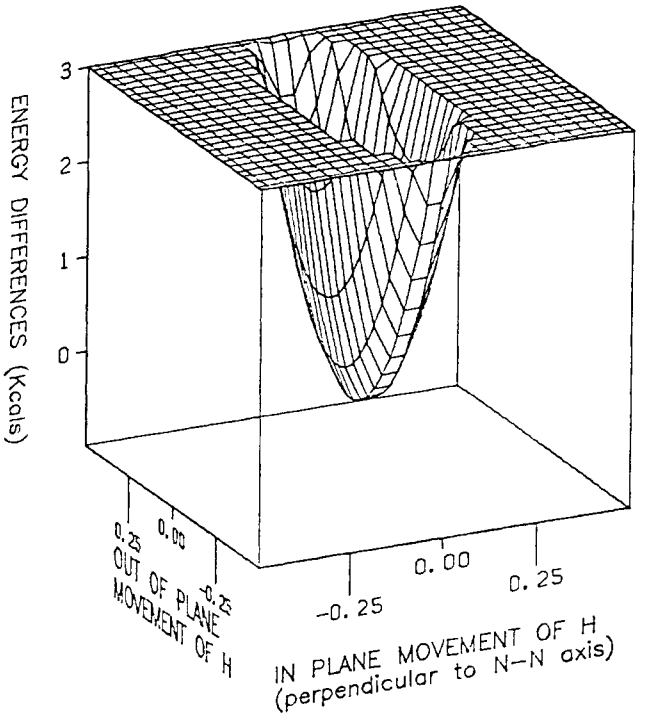

Figure 2. Energy increases caused by proton movement in the X direction (in plane) and in the Z direction (out of plane) from an optimal transition-state geometry.

when confined to the bisecting XZ plane (Figure 1). The resulting transition state has its mobile proton in the N/C/N plane, an energy 21 kcal/mol greater than that of the optimized $NH_2CH_2NH_3^+$ ground state, a partial N–H bond distance of 1.27 Å (compared to 1.01 Å for a primary amine), and a highly nonlinear N/H/N angle of 103°.

Once having located the minimum energy point in the XZ plane, we moved the mobile proton in increments along the X, Y, or Z axis. At each step, the bond distances and angles were optimized to achieve minimal energy for that particular proton locus. For proton movement in the Z direction, calculations were carried out in two ways: (1) Energies were determined without any geometric constraints, thereby permitting rotation about the N–C bonds to accommodate, to whatever extent it can, the proton shift. (2) Energies were also calculated while confining the amino groups to the transition-state geometry; we could thus assess transition-state flexibility in the Z direction when the proton "rides the stationary orbitals". The results of these calculations are given in Table I and Figure 2. The last column of Table I shows how proton relocation affects the energy relative to that of the transition state. There clearly exists a striking insensitivity of the energy to shifts in the mobile proton. For example, a large 0.07-Å proton shift in the XY plane along the $+X$ direction (away from the carbon) or in the $-X$ direction (toward the carbon) raises the energy by less than 1 kcal/mol. Similarly, moving the proton 0.20 Å out of the XY plane along the Z axis produces an energy increase of only 1.1 kcal/mol. Stretching an N–H partial bond 0.15 Å along the N–H vector (not shown in Table I) costs only 0.45 kcal/mol. When the proton shifts 0.20 Å toward one of the nitrogens in the Y direction, the system is stabilized by a mere 1.7 kcal/mol. We conclude that the proton has considerable motional freedom in the transition state even when the system is highly strained. The transition state is, in other words, surprisingly plastic.[6] Calculations of "bond breakage in transition states" to two significant figures would seem akin to citing "43" as the "age" of a human population.

Table I. Transition-State Geometries and Energies for N-to-N Proton Transfer in $NH_2CH_2NH_3^+$ with the Proton Situated at Various Loci

	N–H, Å	N/H/N, deg	N/C/N, deg	ΔE, kcal/mol
TS[a]	1.27	103	88	0.00
$+X$, Å				
0.05	1.30	100	88	0.46[b]
0.07	1.31	98	88	0.89
0.10	1.33	96	88	1.8
0.15	1.37	93	88	4.0
$-X$, Å				
0.05	1.25	107	88	0.46
0.07	1.24	109	88	0.91
0.10	1.23	112	88	1.9
0.15	1.21	116	89	4.1
Y, Å				
0.05	1.31	103	88	−0.15
0.10	1.36	104	88	−0.56
0.15	1.40	104	89	−1.13
0.20	1.44	105	90	−1.67
Z, Å				
0.05	1.28	103	88	0.07[c] (0.16)[d]
0.10	1.28	103	88	0.27 (0.61)
0.15	1.28	102	88	0.61 (1.38)
0.20	1.29	102	88	1.10 (2.45)

[a] Transition state with an energy of 163 kcal/mol compared to 142 kcal/mol for ground state. [b] Indicates that a 0.05-Å shift in the $+X$ direction (see Figure 1) elevates the energy relative to the lowest energy configuration by 0.46 kcal/mol. [c] Energy when permitting complete freedom to optimize. [d] Energy when the atoms of the NH_2 groups are confined to the transition-state coordinates.

Although intermolecular proton transfers are usually considered to have linear geometries[7,8] the N/H/N angle in our intramolecular transition state deviates over 76° from linearity (Table I).[9] This departure from linearity does not, however, seem to contribute substantially to the high 21 kcal/mol activation energy. The major energy requirement must arise from compressing the N/C/N angle from 114.8° in the ground state to 87.9° in the transition state, which, calculations show, requires 20 kcal/mol. Another indication that bent N/H/N geometries cost little derives from calculations on proton transfer in $NH_2CH_2CH_2NH_3^+$. The five-membered cyclic transition state, with a bent N/H/N angle of 134°, is associated with an energy only 5.3 kcal/mol above the ground state. Indeed, no energy is required for proton transfer in $NH_2(CH_2)_3NH_3^+$; the six-membered cyclic transition state has an N/H/N angle deviating 47° from linearity. The im-

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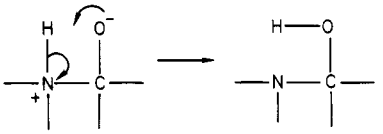
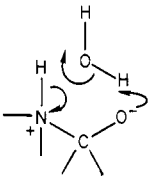
portant point here is that if severely bent N/H/N geometries are readily generated in intramolecular reactions, then nonlinear transfer probably contributes to intermolecular reactions as well.[10] Assumptions of linearity in the latter may therefore be suspect.

The MINDO/3 calculations on $NH_2CH_2NH_3^+$ relate to the "proton switch" mechanism of tetrahedral intermediates:



Such a mechanism has been proposed for ester aminolyses, amide hydrolyses, and enzyme-catalyzed mechanisms.[11-13] It appears from the high activation energy associated with our 1,3-shift that the mechanism, taken literally, is not favorable. If, however, one or more solvent or buffer species intervene according to a Grunwald-Meiboom mechanism,[14] then compressing the N/C/N angle would no longer be necessary, and rates of 10^6-10^8 s^{-1} are possible.



Acknowledgment. This work was supported by the National Science Foundation and the National Institutes of Health. One of the authors (D.C.L.) gratefully acknowledges support from the Alfred P. Sloan Foundation and from the Camille and Henry Dreyfus Teacher-Scholar program.

Registry No. $NH_2CH_2NH_3^+$, 62901-70-6.

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Communications

Stereospecific Synthesis of α,β-Dehydroamino Acids from β-Hydroxy α-Amino Acid Derivatives

Summary: A series of protected β-hydroxy α-amino acids have been converted stereospecifically to their dehydro derivatives by treatment with (diethylamino)sulfur trifluoride and pyridine, threo isomers giving rise to the *Z* derivatives and erythro isomers to the *E* derivatives.

Sir: Dehydroamino acids have recently become a topic of increasing interest as important constituents of many fungal metabolites with antibiotic or phytotoxic properties such as nisin and subtilin.[1,2] In addition, dehydroamino acids are versatile precursors for the asymmetric synthesis of amino acids and peptides.[3-5]

Several syntheses of dehydroamino acids have been reported,[2] the most general of which involves β elimination from β-functionalized α-amino acids. For exammple, β-hydroxy α-amino acids have been converted to their unsaturated analogues via base treatment of their *O*-tosyl or β-chloro derivatives.[6,7] Alternatively, β-mercapto α-amino acids have been oxidized to the corresponding sulfoxides and then subjected to thermal elimination.[8] Direct methods involving dehydration of protected β-hydroxy α-amino acids with several dehydrating agents have also been reported.[9,10] However, mixtures of geometrical isomers (*E* and *Z*) have been obtained. Recently the use of disuccinimido carbonate for the dehydration of threonine to the *Z* isomer has also been reported.[11]

In this paper we describe a one-step, stereospecific and efficient method for the preparation of α,β-dehydroamino acids from protected β-hydroxy α-amino acids using (diethylamino)sulfur trifluoride (DAST) with pyridine as the dehydrating agent. Although DAST is generally employed for fluorinating alcohols with a minimum of side reactions,[12] a few instances involving extensive dehydration have been reported.[13,14] We have thus investigated dehydration of β-hydroxy amino acid derivatives with DAST, and we have found that in the presence of a base such as

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