ordinates, the partial derivatives at the new position are recalculated, and from the six partial derivatives for the two values of each coordinate, the constants in the energy equation (A–F) are calculated. The derivative of this equation is then set equal to zero, which gives the position of minimum energy, and the atom is placed at that point. The program then repeats the procedure for the next atom, and this process is continued until all atoms have had their positions of minimum energy calculated sequentially, and the atoms have been repositioned. The calculations are then repeated in their entirety, using the new set of coordinates as a starting point. This process is continued until the atomic motions are judged to be sufficiently small, and that it is not worthwhile to proceed. In practice, the allowable errors are usually on the order of 0.001 Å in each coordinate. Following the idea introduced originally by Wiberg, when a carbon atom is moved, the attached hydrogen atoms (or other attached atoms such as halogen) are moved along with it. The hydrogens are then allowed to seek their own minima holding the carbon constant.

Magnetic Nonequivalence in the Low-Temperature Nuclear Magnetic Resonance Spectra of *N*-Benzyl-*N*-methylhydroxylamine and *N*-Benzyl-*N*-methylchloramine[1]

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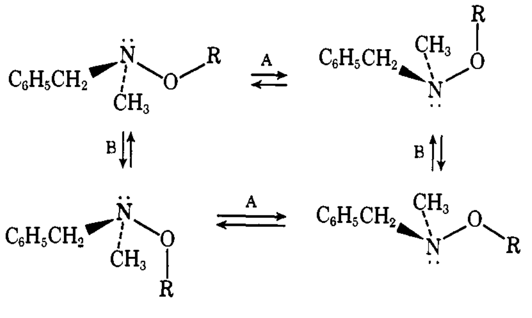
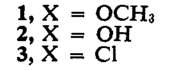
Abstract: Reinvestigation of the low-temperature nmr spectra of *N*-benzyl-*N*-methylhydroxylamine and *N*-benzyl-*N*-methylchloramine in acetone-d_6 at 100 MHz has revealed magnetic nonequivalence. The slow process with the *N*-chloro compound must be nitrogen inversion. The fact that, in acetone-d_6, *N*-benzyl-*N*-methylhydroxylamine undergoes degenerate racemization more slowly than *N*-benzyl-*O,N*-dimethylhydroxylamine supports the hypothesis that inversion of nitrogen is slower than the rate of rotation about the N–O bond in these compounds.

Since observation of magnetic nonequivalence in the low-temperature nmr spectra of some hydroxylamine derivatives[2] there has been controversy surrounding the nature of the measured rate process. In the case of cyclic hydroxylamines there appears to be general agreement that magnetic nonequivalence results from restricted pyramidal inversion at nitrogen;[3–5] however, in acyclic derivatives the possibility that the rate-determining step reflects a substantial barrier to rotation about the N–O bond must also be considered.[6–8]

Degenerate racemization of a benzylhydroxylamine requires both inversion at nitrogen (process A) and rotation about the N–O bond or its equivalent, inversion at oxygen (process B). If either A or B is slow on the nmr time scale, in principle, magnetic nonequivalence of the benzyl CH_2 protons will result. In fact, the observation of a small steric deceleration has been interpreted as evidence for a torsional barrier as the measured process.[8c]



We had previously reported[2a] that, although *N*-benzyl-*O,N*-dimethylhydroxylamine (**1**) exhibited magnetic nonequivalence of the benzyl hydrogens at readily accessible temperatures, neither *N*-benzyl-*N*-methylhydroxylamine (**2**) nor *N*-benzyl-*N*-methylchloramine (**3**) showed such nonequivalence. In light of the



$$C_6H_5CH_2\text{—}\underset{\displaystyle CH_3}{\underset{|}{N}}\text{—}X$$

1, X = OCH_3
2, X = OH
3, X = Cl

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demonstrated ability of an *N*-chloro substituent to stabilize the pyramidal form of aziridines,[9] equivalence of the CH_2 protons in **3** appeared to confirm the idea that nitrogen inversion was not the measured rate process for **1**. Furthermore, equivalence in **2** could be interpreted as evidence for a torsional barrier which is lowered by replacement of a methyl group by the much smaller proton.[10]

In order to resolve these apparent inconsistencies, we have reinvestigated the spectra of **2** and **3** at higher resolution. This seemed especially pertinent in light of the nonequivalence reported for *N*,*N*-dibenzylhydroxylamine in deuteriochloroform and deuteriomethanol.[11]

Results and Discussion

Reinvestigation of the spectra of **1**, **2**, and **3** at 100 MHz in acetone-d_6 shows that all exhibit magnetic nonequivalence at low temperatures. Furthermore, in this solvent, both **2** and **3** show free energies of activation which are larger than for **1** (Table I). Determination of the Arrhenius activation parameters by the use of computer-simulated spectra[2a] indicated even larger differences in the energies of activation (E_A).

Table I. Spectral Parameters in Acetone-d_6 at 100 MHz

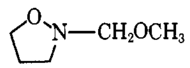
Compd	T_c,[a] °C	$\nu_A - \nu_B$, Hz	J_{AB}, Hz	$\Delta G_c^{\ddagger}$,[b] kcal/mol	E_A, kcal/mol	log A
1	−83	8.8	13.2	9.9	8.3	11.0
2	−35	6.1	12.6	12.4	13.5	13.9
3	−66	26.1	11.2	10.3	11.8	14.2

[a] Coalescence temperature. [b] Calculated at T_c in the manner previously described.

Because nitrogen inversion in *N*,*N*-dibenzylmethylamine is characterized by a free-energy barrier of 6 kcal/mol at −146°,[12] it is evident that the barrier to exchange is substantially increased by substitution by either oxygen or chlorine. In the chloramine, magnetic nonequivalence must arise as the result of slow inversion of nitrogen, because the angle of rotation about the N–Cl bond is undefined.

Of the hydroxylamines, **2** would be expected to show a smaller steric acceleration ("B-strain effect") than **1** on process A. If the measured exchange were the result of a torsional barrier to rotation about the O–N bond (process B), **2** is expected to undergo degenerate racemization more rapidly than **1**.[8c] The observation of a 3 kcal larger barrier for **2** is consistent with the previously observed steric effects on inversion of the nitrogen pyramid in aziridines.[13,14]

The small deceleration observed[8c] upon substitution of the methyl substituents in **1** by isopropyl groups is difficult to interpret in the absence of knowledge of the preferred conformations of these compounds. Because the effective steric differences might, in fact, be small, it is possible that electronic differences between methyl and isopropyl could be more important in determining the rate of nitrogen inversion. There is some evidence that electronic factors may be important because both **4** and **5** undergo inversion more rapidly than their *N*-alkyl analogs.[5b,15] We are currently investigating this possibility in more detail.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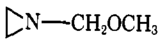
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Experimental Section

The compounds were prepared as previously described.[2a] Spectra were determined on a Varian HA-100 instrument equipped with a variable temperature probe. Temperature calibration was accomplished by measurement of the methanol chemical shifts, and temperatures are believed to be accurate to ±2°.

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