NUCLEAR MAGNETIC RESONANCE STUDY OF RESTRICTED ROTATION

IN 1-TERT-BUTYL-N,N,2,2-TETRAMETHYLPROPANAMINE

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Studies of nitrogen inversion and rotation about the C-N bond by the dynamic NMR method (DNMR) have been the subject of many recent publications (1). These studies have shown that, for the compounds studied to date, the activation parameters are not very sensitive to the extent of steric hindrance around the amino group, and that C-N bond rotation and nitrogen inversion generally occur at comparable rates. The subject of this note is a DNMR study of the highly hindered 1-tert-butyl-N,N,2,2-tetramethylpropanamine (TBTP).

The free energy of activation is found to be significantly greater than published values for similar, but sterically less hindered, compounds.

TBTP is obtained in good yield by radical processes from the reaction of t-butyllithium with either N,N,N'N'-tetramethylchloroformamidinium chloride or N,N,N'N'-tetramethylformamidium chloride (2). Proton NMR spectra of 20% v/v solutions of TBTP in d_5-pyridine were obtained at 100 MHz nominal proton frequency with a Varian HA100 spectrometer. Spectra were recorded at 5° temperature intervals between -20 and $+120^o$C using a Varian variable temperature unit; temperatures were maintained at $\pm1^oC$. Full lineshapes of the N-methyl protons were recorded under slow passage conditions after complete temperature equilibration.

Over the entire studied temperature range, sharp and immovable singlet peaks were observed at 2.07 and 1.03 ppm for the methine and t-butyl protons, respectively. In the range $-20 \leq T \leq 40^oC$, the N-methyl groups gave rise to two equally intense triplet absorptions with chemical shifts of 2.55 and 2.59 ppm. The amplitude ratio of the triplet lines was 7:10:7 and the peak separation was 0.65 Hz; scalar nitrogen coupling accounts well for both of these observations (3,4). Above 40^oC the scalar coupling disappeared concurrently with broadening and finally coalescence ($T_c = 62^oC$) of the N-CH_3 absorptions into a single peak. This effect was perfectly reversible. Although we did not study it in detail, we observed a similar exchange phenomenon in benzene and toluene solutions, but not in methyl-cyclohexane nor acetone solutions.

To better understand the dynamics of the N-methyl exchange, we performed a total lineshape analysis of the spectra recorded between 45 and 120°C with the help of computer program DNMR (5) which was modified by the addition of an iteration subroutine based on the simplex algorithm of Nelder and Mead (6). Since the scalar H-N coupling was not resolved in this temperature region we have assumed that residual inhomogeneous broadening was taken care of by an appropriate transverse relaxation time, T_2'. Slight deviations between calculated and experimental lineshapes in the 40-50°C range can be attributed to this approximation, since inhomogeneously broadened lines are partially Gaussian, while the computer program assumes Lorentzian lines (7).

The computer calculations were performed for mutual exchange of two spins between two environments, and the simulated spectra were plotted with a Calcomp plotter. Some results are shown in Figure 1. We obtained $E_a \simeq 26.3$ Kcal/mole and $\Delta F^{\ddagger} = 18.5 \mp 0.2$ Kcal/mole at the coalescence temperature, $Tc = 62°C$.

The $\Delta F^{\ddagger}$ reported here is, to our knowledge, the largest ever published for rotation around the C-N bond and is close to values for rotation around partial double bonds, as in amides. Typically, values of $\Delta F^{\ddagger}$ of the order of 6 Kcal/mole have been observed for amines.

The rate process can best be accounted for by considering the equilibration between the preferred conformations, 1a-b. In this representation the t-butyl groups are equivalent, as observed. Examination of space-filling molecular models shows that the molecule is sterically
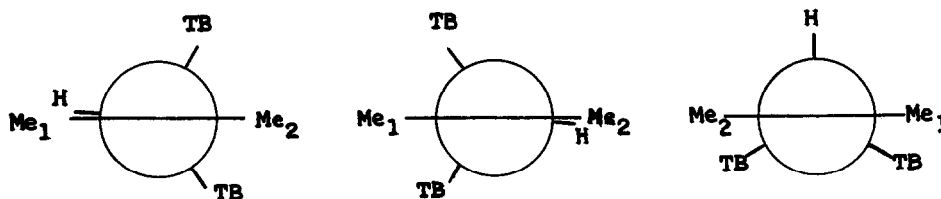
extremely crowded, but that conformation 1, in which one N-methyl group is nestled between the tert-butyl groups and the other is staggered between a tert-butyl group and the methine proton, is no more crowded than conformation 2.

The Newman projections have been drawn here with nitrogen sp^2 hybridized with the N-methyl groups coplanar (or nearly coplanar). Such arrangement is consistent with the observations of resolved nitrogen scalar coupling. This effect is unexpected for a molecule of apparently low nitrogen site symmetry, but can be ascribed precisely to this arrangement. This geometry will lead to a reduction of the quadrupole energy and, therefore, by virtue of a classical relation (8), to a sufficiently long spin lattice relaxation time T_1, such that $T_1 > J/h$, where J is the scalar coupling constant.
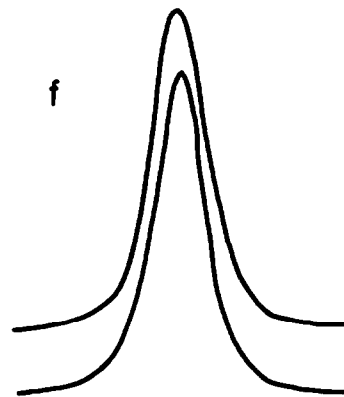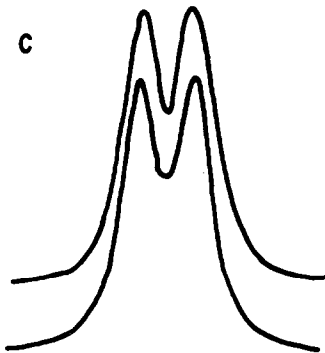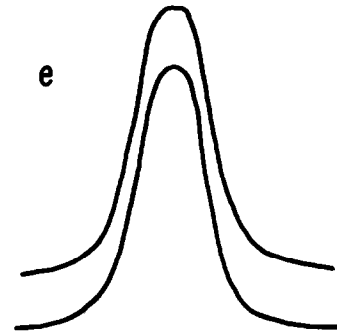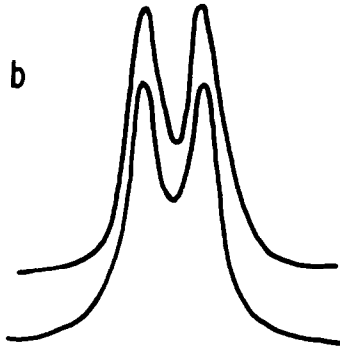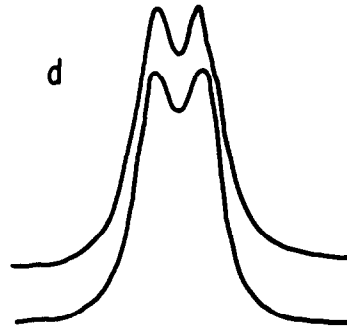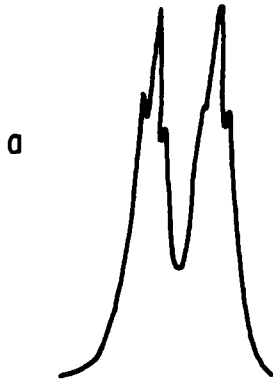
References and Notes

1.   For a review on the subject see for instance

    a.   C. H. Bushweller, W. G. Anderson, P. W. Stevenson, D. L. Burkey, J. W. O'Neil,
        J. Amer. Chem. Soc., 96, 3892 (1974);

    b.   J. Reny, C. Y. Wang, C. H. Bushweller, W. G. Anderson, Tetrahedron Lett., 8,
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3.   J. A. Pople, Molecular Phys., 1, 168 (1959).

4.   E. D. Becker, H. T. Miles, R. B. Bradley, J. Amer. Chem. Soc., 87, 5575 (1965).

5.   G. Binsch, D. A. Kleier, Quantum Chemical Program Exchange #140 (1969).

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7.   The Hamiltonian subroutine in program DNMR could be modified for inclusion of scalar
    coupling, however, since one would also introduce a new variable, it is questionable
    that the overall calculations would benefit from it.

8.   W. B. Moniz, H. S. Gutowsky, J. Chem. Phys., 38, 1155 (1963).