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# DIRECT OBSERVATION OF AN UNUSUALLY HIGH BARRIER TO ROTATION ABOUT A CARBON-NITROGEN SINGLE BOND IN t-BUTYLDIMETHYLAMINOBORANE

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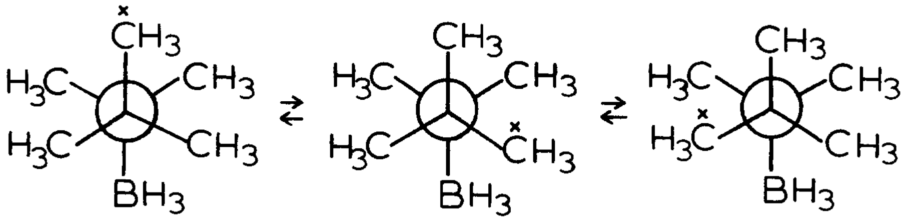
Although there exists a large amount of data regarding the barrier to rotation about carbon-nitrogen bonds possessing greater than single-bond order,[1] relatively little information is available concerning rotation about legitimate carbon-nitrogen single bonds. Microwave spectroscopy has revealed rotational barriers in $CH_3NH_2$ ($\Delta H^{\ddagger}$ = 2.0 kcal/mole)[2], $(CH_3)_3N$ ($\Delta H^{\ddagger}$ = 4.4 kcal/mole)[2], and $CH_3NO_2$ ($\Delta H^{\ddagger}$ = .006 kcal/mole)[2] while nmr spectroscopy gave the rate of t-butyl rotation in t-butyldimethylamine ($\Delta H^{\ddagger}$ = 6.2 kcal/mole)[3]. In addition, there are very few reports of the observation of nonequivalence in the t-butyl group.[4,5]

This report concerns the observation of nonequivalence in t-butyl of t-butyldimethylaminoborane(I) revealing a dramatic increase in the barrier to t-butyl rotation as compared to t-butyldimethylamine.[3]

Examination of the pmr spectrum (60 MHz) of I in $CH_2CHCl$ at about room temperature revealed two singlet resonances for the t-butyl ($\delta$1.29) and $N(CH_3)_2$ ($\delta$2.47) groups. The pmr resonances due to the $BH_3$ protons are not evident at the signal amplification used due to significant quadrupole-induced broadening.[6]

Upon lowering the temperature, the t-butyl resonance (Figure 1) broadened in a manner characteristic of a decreasing rate of exchange on the pmr time scale giving finally two singlet resonances at $\delta 1.36$ and $\delta 1.16$ with a respective relative area ratio of 2:1. The smaller resonance at $\delta 1.16$ has a slightly greater $W_{1/2}$ than the larger peak at $\delta 1.36$. The $N(CH_3)_2$ resonance was essentially independent of temperature. No other changes in the spectrum were observed down to -156°.

These spectral changes can be best rationalized by a slowing of rotation about the t-butyl-nitrogen bond (eq 1; Newman projection looking down the central



(1)

t-butyl carbon-nitrogen bond). Perusal of eq 1 indicates that in any of the three equivalent rotamers the N-methyl groups always experience equivalent environments and should display a pmr spectrum independent of any rate process except $CH_3$—N rotation. However, for the t-butyl group in any given rotamer (eq 1), there are two equivalent methyls bisected by the $BH_3$ group and one other methyl which bisects the $N(CH_3)_2$ group. In the event of slow t-butyl rotation (eq 1), the t-butyl resonance should consist of two singlets of 2:1 relative area ratio as observed (Figure 1). In addition, it is clear (eq 1) that the three methyls of the t-butyl group do indeed exchange environments via rotation and that rapid rotation on the pmr time scale will result in a singlet resonance. A total pmr line shape analysis at -80° (Figure 1) gives $\Delta G^{\ddagger} = 9.7 \pm 0.3$ kcal/mole for t-butyl rotation.

A possible alternative rationalization of the spectral behavior reported above involves an inherently high barrier to rotation (>10 kcal/mole) in I with dissociation of I to the free amine (in which rotation is very rapid[3]) being the rate-determining step in the process rendering all t-butyl methyls equivalent.

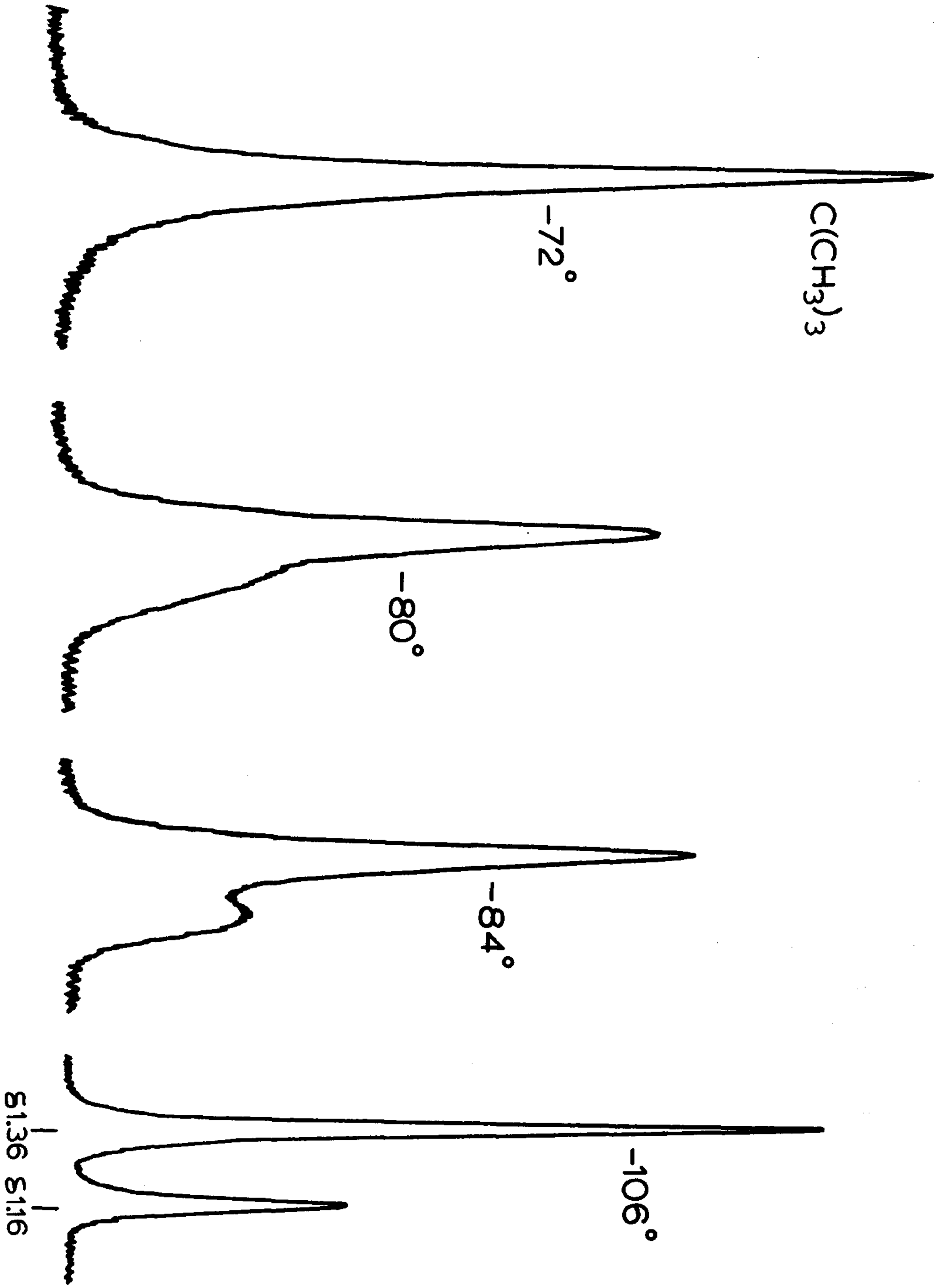


Figure 1

However, the rate of such a dissociative process should depend on the concentration of free amine. The addition of a molar equivalent of t-butyldimethylamine to the sample used above did not produce any changes whatsoever in the spectral behavior of I. Indeed, the t-butyl resonance due to the free t-butyldimethylamine ($\delta$1.03) remained very sharp over this temperature range providing strong evidence against a dissociation process.

Although the barrier to rotation in I is substantially higher (~4 kcal/mole) than in t-butyldimethylamine,[3] it would not be reasonable to extract any quantitative trends regarding vicinal eclipsing interactions in these two compounds because rotation may occur by a different mechanism in each case. In the case of free t-butyldimethylamine, rotation and inversion may share the same transition state, i.e., a planar ($sp^2$) configuration at nitrogen.[7] However, in I, complexation by $BH_3$ prevents any inversion process at nitrogen and the most reasonable transition state is the eclipsed form analogous to ethane.

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## REFERENCES

(1) C. H. Bushweller, P. E. Stevenson, J. Golini, and J. W. O'Neil, J. Phys. Chem., 74, 1155 (1970) and references therein.

(2) E. B. Wilson, ~~Jr.,~~ Advan. Chem. Phys., 2, 367 (1959); D. J. Millen, Progress in Stereochemistry, 3, 138 (1962).

(3) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, J. Amer. Chem. Soc., 92, 6349 (1970).

(4) W. E. Heyd and C. A. Cupas, ibid., 91, 1559 (1969).

(5) F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, ibid., 90, 5243 (1968).

(6) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, ibid., 92, 3484 (1970); M. Grace, H. Beall, and C. H. Bushweller, Chem. Comm., 701 (1970).

(7) A. Rauk, L. C. Allen, and K. Mislow, Angew. Chem. internat. Edit., 9, 400 (1970).