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THE EFFECT OF PYRAMIDALITY ON ROTATIONAL BARRIERS IN ACYCLIC TRIALKYLAMINES

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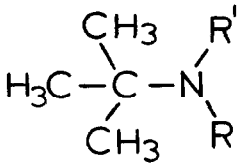
The relative importance of the various factors which determine the barrier to pyramidal inversion about nitrogen is reasonably well established in a variety of heterocycles and in some acyclic systems.[2] However, it has not been clearly established what happens to the rotational barrier in acyclic trialkylamines[3] as alkyl substituent steric bulk increases.

Examination of the ^1H DNMR spectra (60 MHz) of a series of N-tert-butyl-N,N-dialkylamines (1) as 5% v/v solutions in $CBrF_3$ (1b-e,g) or a 7% v/v solution in CH_2CHCl (1a) or a 10% v/v solution in CD_2CDCl (1f)[4] revealed in most cases changes in the tert-butyl resonance at low temperatures attributable to slowing of tert-butyl rotation. Although there were differences in the chemical shift values and widths-at-half-height at low temperatures in the two solvent systems employed, the barrier ($\Delta G^{\ddagger}$) to tert-butyl rotation or nitrogen inversion determined by total line shape analysis for those compounds appreciably soluble in both solvents, e.g., 1d, was independent of solvent within experimental error (±0.2 kcal/mole). The chemical shift values for the nonequivalent methyls



1 (a) R = R' = CH_3

(b) R = CH_3; R' = CD_2CD_3

(c) R = CD_3; R' = CH_2CD_3

(d) R = R' = CH_2CD_3

(e) R = CH_3; R' = $(CD_3)_2CD$

(f) R = CH_3; R' = $CH_2C_6H_5$

(g) R = CH_2CD_3; R' = $(CD_3)_2CD$

of the various tert-butyl groups under slow exchange conditions were obtained from a total line shape analysis and are compiled in Table I. In the case of 1g, no really clear-cut changes in the spectrum occurred although at -185° definite asymmetry is observed in the tert-butyl resonance (TMS Lorentzian). At -188°, the sample of 1g froze.

Table I. ^1H Chemical Shifts (60 MHz) of Nonequivalent Methyls of the tert-Butyl Group in N-tert-Butyl-N,N-dialkylamines

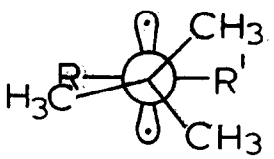
compound	temp, °C	chemical shifts, Hz	solvent
1a	-165°	64.8(6H); 50.3(3H)	CH_2CHCl
1b	-145°	68.6(6H), 51.2(3H)	$CBrF_3$
1c	-145°	68.5(6H); 52.0(3H)	$CBrF_3$
1d	-167°	69.6(6H); 56.5(3H)	$CBrF_3$
1e	-174°	72.0(3H); 67.0(3H); 58.0(3H)	$CBrF_3$
1f	-151°	76.7(3H); 66.6(3H); 60.0(3H)	CD_2CDCl

Taking into account the variations in T_2 with temperature for 1a, 1b, 1c, and 1f using a method described previously[3a] or using model compounds, e.g., 1b for 1c, and assuming the chemical shifts of the tert-butyl resonances to be independent of temperature as has been observed previously in the case of 1a[3a], free energies of activation ($\Delta G^{\ddagger}$) for tert-butyl rotation were determined by the total line shape method and are compiled in Table II. Since no unequivocal changes occurred for the DNMR spectrum of 1g, we are able to assign only an upper limit to the tert-butyl rotational barrier in 1g. It

Table II. Free Energy of Activation ($\Delta G^{\ddagger}$) for tert-Butyl Rotation and Net Nitrogen Inversion in N-tert-Butyl-N,N-dialkylamines

compound	temp, °C	$\Delta G^{\ddagger}$ (tert-butyl rotation), kcal/mole	$\Delta G^{\ddagger}$ (inversion), kcal/mole
1a	-153°	6.0±0.1	——
1b	-130°	7.1±0.1	——
1c	-130°	7.1±0.1	7.2±0.2
1f	-138°	6.2±0.2	6.2±0.2
1d	-160°	5.7±0.2	5.8±0.2
1e	-167°	5.6±0.2	——
1g	-185°	$\leq$4.4	$\leq$4.4

is noteworthy that the barriers ($\Delta G^{\ddagger}$) to net nitrogen inversion in 1c, 1d, and 1f as revealed by the CH_2 resonances separating into AB spectra are essentially identical to the respective tert-butyl rotational barriers (Table II) again consistent with a high degree of cooperativity between the rotation and inversion processes.[4] Such behavior is consistent with but not unequivocal proof for a common transition state (2) for tert-butyl rotation and nitrogen inversion[4] in the series 1. Perusal of Table II indicates first an increase in the free energy of activation ($\Delta G^{\ddagger}$) for tert-butyl rotation in going from 1a to 1b or 1c and then a progressive decrease as the steric bulk of the alkyl substituents increases. Using the common transition state model, as the steric bulk of the N-alkyl substituents increases, the pyramidality about nitrogen should decrease and the contribution to the tert-butyl rotational barrier due to nitrogen rehybridization should decrease.[4] Indeed, the barrier to nitrogen inversion should also decrease as is observed. In a comparison between 1a and 1b or 1c, examination of models indicates no significant increase in nonbonded repulsions in the pyramidal ground state of 1b or 1c as compared to 1a, i.e., similar pyramidalities, due to the ability of the ethyl group to rotate into conformations which minimize nonbonded repulsions. However, in 1c, rendering the diastereotopic CH_2 protons isochronous on the NMR time scale requires not only nitrogen inversion but also CH_2–N bond rotation. Thus, there may well be a significant



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torsional contribution to the observed barrier for the net inversion process in 1c. This would lead, of course, to a higher barrier to the net inversion process in 1c than in 1a and a concomitant increase in the tert-butyl rotational barrier using the coupled inversion-rotation model as is observed (Table II). Indeed, this rationale may be applied to all of the compounds in series 1. However, subsequent increases in the steric bulk of the N-alkyl substituents then lead to a progressive decrease in the tert-butyl rotational barrier (Table II) consistent with an ever-decreasing pyramidality resulting in a decreasing rehybridization contribution to the tert-butyl rotational barrier. While net rotation of tert-butyl may be assumed to have 3-fold character in 1a, the apparently significantly reduced pyramidality in more hindered amines, e.g., 1g, imparts a significant degree of 6-fold character to tert-butyl rotation and lowers the barrier.

Thus, it is apparent from the above data that not only barriers to nitrogen inversion but also barriers to C–N bond rotation are a functtion of pyramidality about nitrogen in acyclic trialkylamines. The trend observed for the series 1 is in contrast to the generally observed increase in rotational barriers for acyclic hydrocarbons as substituent steric bulk increases.[3bc]

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