Ethyl-group Rotational Barriers in Hindered Trialkylamines. A Dynamic NMR and Molecular Mechanics Investigation[1]

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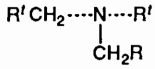
The stereodynamics of *N*-ethyl-*N*-*tert*-butylneopentylamine **2** and three similar compounds **3–5**, are reported and discussed. Dynamic NMR spectroscopy yields experimental barriers to nitrogen inversion–rotation, N–*tert*-alkyl bond rotation and N–ethyl bond rotation for **2** of 8.1, 7.3 and 6.0 kcal mol^{-1}, respectively, and shows that two different conformations about the latter bond are populated in the ratio 9:1. Molecular mechanics calculations fit well with these observations indicating which these conformations are and yielding a calculated ethyl group rotation barrier in good accord with experiment. Comparable results are obtained for the other three compounds.

The carbon–nitrogen bond in simple alkylamines is *ca.* 7 pm shorter than the carbon–carbon bond in the corresponding alkane,[2,3] so interactions of substituents at opposite ends of the bond are somewhat greater. On the other hand, the barrier to rotation in methylamine,[4] 1.98 kcal mol^{-1}, is *ca.* 0.9 kcal mol^{-1} smaller than that in ethane,[5] so the rotational barriers in alkylamines should reflect these contrasting influences.

In simple ethylamines,[6] barriers to rotation of ethyl groups, *i.e.* about the N–C bond, are in the range 5–6 kcal mol^{-1}, see Table 1, while the barrier to rotation about a C–ethyl bond has been measured by dynamic NMR spectroscopy in only one† saturated hydrocarbon, 2,2-dimethylbutane,[8] and it is only 4.9 kcal mol^{-1}. In the less crowded hydrocarbons corresponding to the ethylamines studied, barriers are expected to be smaller, so in these amines the shorter C–N bond does give higher rotational barriers.

In contrast, rotations of *tert*-butyl groups in *tert*-butylamines have barriers[9] which are more often smaller than in the corresponding hydrocarbons[8,10,11] as the examples in Table 1 show. Interactions of the *tert*-butyl group in staggered ground-state conformations are significant, so depending whether the relatively short C–N bond affects interactions in the ground state more or less than those in the transition state, the N–*tert*-butyl rotation barrier will be lower or higher than in the corresponding hydrocarbon.


$\mathrm{R^tCH_2{\cdots}\underset{CH_2R}{N}{\cdots}R^t}$

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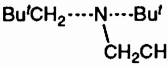
$\mathrm{Bu^tCH_2{\cdots}\underset{CH_2CH_3}{N}{\cdots}Bu^t}$

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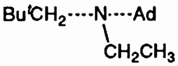
$\mathrm{Bu^tCH_2{\cdots}\underset{CH_2CH_3}{N}{\cdots}Ad}$

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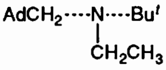
$\mathrm{AdCH_2{\cdots}\underset{CH_2CH_3}{N}{\cdots}Bu^t}$

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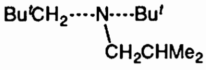
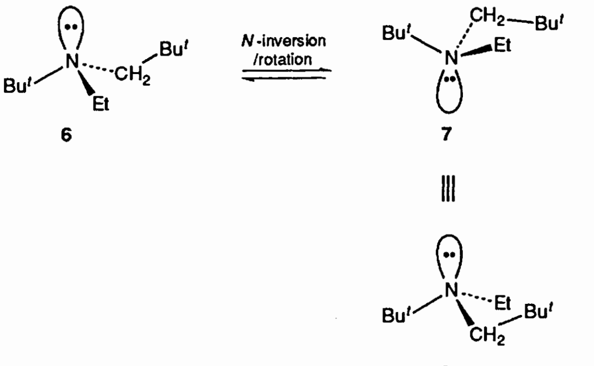

$\mathrm{Bu^tCH_2{\cdots}\underset{CH_2CHMe_2}{N}{\cdots}Bu^t}$

5

R^t = *tert*-alkyl
Ad = adamantyl

We have recently been investigating amines in the series **1**,[12] in the expectation that the strong commitment to an *anti*-conformation of the *tert*-alkyl groups will lead to unusual conformational behaviour. We now report dynamic NMR measurements and molecular-mechanics calculations for the ethylamines **2–4**, and for **5**, an analogue of **2**, in which the ethyl group is replaced by an isobutyl group.



6 **7** **8**

Such amines can exist in two enantiomerically related configurations **6** and **7** (= **8**) linked by nitrogen inversion–rotation, and within each configuration the usual rotational possibilities for each alkyl group may lead to a range of different conformations being populated. Past experience suggests[1,6,9,12–16] that both nitrogen inversion–rotation and some alkyl-group rotations should be slow on the NMR timescale at low temperatures. The nature of the changes in the spectrum and the calculations should allow elucidation of the conformational picture.

Results and Discussion

Only compound **2** was soluble down to −165 °C and gave a clear-cut set of changes. The results for **3**, **4** and **5**, as far as they were obtained, seemed to be similar to those for **2**. NMR spectral changes for each compound are summarised in Tables 2 (^{1}H) and 3 (^{13}C) but those for ethylamine, **2**, will now be described in detail.

The room-temperature ^{1}H NMR spectrum of **2** comprises two *tert*-butyl singlets, a methylene singlet and a typical quartet and triplet for the ethyl group. Below *ca.* −40 °C the methylene signals broaden, and split below *ca.* −100 °C to give an AB system for the neopentyl methylene group and two multiplets for the ethyl methylene group at −120 °C. Geminal protons have become diastereotopic owing to nitrogen inversion–rotation $\mathbf{6} \rightleftharpoons \mathbf{7}$ becoming slow on the NMR timescale.

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† Rotation about an sp^3 carbon–ethyl bond has been reported for a tryptocene derivative.[7]

Table 1 Barriers (kcal mol^{-1}) to rotation[a] about the N–ethyl bond in substituted ethylamines R^{1}R^{2}N–CH$_2$CH$_3$, about the N–*tert*-butyl bond in substituted *tert*-butyl amines R^{3}R^{4}N–CMe$_3$ and about the C–*tert*-butyl bond in substituted neopentyl hydrocarbons R^{3}R^{4}CH–CMe$_3$

				Amines		Hydrocarbons	
R^1	R^2	R^3	R^4	N–Et rotation	Ref.	C–Et rotation	Ref.
Me	Et			5.2; 5.9	6	—	
Et	Et			6.0; 6.3	6	—	
				N–Bu^t rotation		C–Bu^t rotation	
		Me	Me	6.2	9	6.9	8, 10
		Me	Et	7.1–7.3	9	6.3	8
		Me	Pr^i	5.5	9	6.0	8
		Me	CH$_2$Ph	6.3	9	7.1	11

[a] Rotation means interconversion of two rotational conformers separated by a degree of rotation which varies from compound to compound, as the original work describes, and which may be accompanied by more or less rotation of other groups. For the first two entries, two such interconversions are observed (see ref. 6).

Table 2 ^{1}H Chemical shifts (400 MHz) of compounds **2–5** at various temperatures (ppm from Me$_4$Si)

Compound	T/°C	NCH_2–CH$_3$	NCH_2–Cq	CH_3–CH$_2$N	CH_3–CqN	CH_3–CqCH$_2$		
Bu^{t}CH$_2$N(Bu^t)CH$_2$CH$_3$	−50	2.71	2.37	1.21	1.16	1.02		
2	−140	3.07; 2.42	2.62; 2.14	1.22	1.26; 1.20; 1.09	1.02		
		NCH_2–CH$_3$	NCH_2–Cq	CH(Ad)	CH_2(Ad)	CH_2(Ad)	CH_3–CH$_2$N	CH_3–CqCH$_2$
Bu^{t}CH$_2$N(Ad)CH$_2$CH$_3$	+25	2.72	2.35	2.11	1.77	1.71	1.13	0.94
3	−110	3.17; 2.30	2.70; 2.02	2.15	1.79; 1.72	1.67	1.15	0.94
	−135			2.17; 2.12; 2.12	*a*	*a*		
		NCH_2–CH$_3$	NCH_2–Cq	CH(Ad)	CH_2(Ad)	CH_2(Ad)	CH_3–CH$_2$N	CH_3–CqN
AdCH$_2$N(Bu^t)CH$_2$CH$_3$	+25	2.55	2.1	1.94	1.67	1.50	1.07	1.0
4	−115	2.83; 2.18	2.26; 1.82	1.89	1.59	1.41	1.01	0.95
		NCH_2–CH	NCH_2–Cq	CH–CH$_2$N	CH_3–CqN	CH_3–CH	CH_3–CqCH$_2$	
Bu^{t}CH$_2$N(Bu^t)CH$_2$–Pr^i	−67	2.18	2.11	1.73	0.98	0.79	0.77	
5	−128	2.61; 1.71	2.36; 1.73	1.71	0.98	0.87; 0.67	0.75	
	−146				0.93; 0.90; 0.80			

[a] At −135 °C these signals split further owing to slow Ad–N rotation but they overlap too much to be assigned unambiguously.

Table 3 ^{13}C Chemical shifts (75.5 MHz) of compounds **2–5** in CHF$_2$Cl at various temperatures (ppm from TMS)

Compound	T/°C		NCH$_2$–Cq	NCq	NCH$_2$–CH$_3$	Cq–CH$_2$	CH$_3$–CqCH$_2$	CH$_3$–CqN	CH$_3$–CH$_2$N		
Bu^{t}CH$_2$N(Bu^t)CH$_2$CH$_3$	−80		63.9	55.6	47.4	32.2	27.8	26.6	18.0		
2	−125		63.9	55.6	47.4	31.6	27.3	30.4; 29.5; 16.8	17.9		
	−165	90%	64.7	55.8	47.8	31.8	26.2	30.0; 30.0; 17.5	17.9		
		10%	57.8	54.1	43.7	—	—	— 23.6; 9.9	—		
			NCH$_2$–Cq	NCq	NCH$_2$–CH$_3$	CH$_2$(Ad)	CH$_2$(Ad)	Cq–CH$_2$	CH(Ad)	CH$_3$–CqCH$_2$	CH$_3$–CH$_2$N
Bu^{t}CH$_2$N(Ad)CH$_2$CH$_3$	−80		61.8[a]	55.8	46.0	39.9	36.7	32.3	29.8	28.2	17.5
3	−138		62.9[a]	56.0	46.4	43.2; 42.7; 31.6	36.2	32.5	29.3	27.8	17.0
			NCH$_2$–Cq	NCq	NCH$_2$–CH$_3$	CH$_2$(Ad)	CH$_2$(Ad)	Cq–CH$_2$	CH(Ad)	CH$_3$–CqN	CH$_3$–CH$_2$N
AdCH$_2$N(Bu^t)CH$_2$CH$_3$	−40		65.2	55.2	47.6	40.9	36.8	33.9	28.3	26.6	17.5
4	−125		64.7[b]	55.4	47.6	40.7	36.5	33.8	28.2	31.0; 29.7; 18.8	17.0[b]
			NCH$_2$Cq	NCH$_2$–CH	NCq	Cq–CH$_2$	CH–CH$_2$	CH$_3$–CqCH$_2$	CH$_3$–CqN	CH$_3$–CH	
Bu^{t}CH$_2$N(Bu^t)CH$_2$–Pr^i	−70		64.4	61.3	55.9	32.1	30.0	28.5	26.9	20.8	
5	−140		64.3	61.0	55.8	32.6	30.0	28.1	31.1; 31.1; 17.9	21.0; 20.1	

[a] The signal at 61.8 splits into a major broad line (62.9) and a minor one (too broad to be detected) owing to slow N–Et rotation. [b] At even lower temperature (−130 °C) these lines are so broad as to disappear, owing to slow N–Et rotation.

Complete lineshape fitting of calculated and experimental spectra suggests that this process occurs 190 and 400 times per second at −101 and −95 °C, respectively, when the free energy of activation is 8.1 kcal mol^{-1}. As expected there is no corresponding change in the ^{13}C NMR spectrum which can be associated with this process.

At *ca.* −100 °C the *N-tert*-butyl ^{1}H NMR signal begins to broaden and it splits below *ca.* −140 °C into three signals of equal intensity. The ^{13}C signal for the same *tert*-butyl methyl groups shows a similar splitting into three, see Fig. 1, corresponding to a barrier to rotation of 7.3 kcal mol^{-1} at −118 °C. No other NMR signals respond to the slowing of this process.

At *ca.* 125 °C in the ^{1}H NMR spectrum, a new broadening of the upfield part of the signal of the ethyl methylene group takes place until below *ca.* −140 °C ill-defined splitting is observed. Changes are more clearly observed in the ^{13}C NMR spectrum, showing two signals in the approximate ratio 9:1 for all groups at −165 °C, see Fig. 1. Complete lineshape treatment yields a barrier of 6.0 kcal mol^{-1} for the exchange of the molecule

Table 4 Free energies of activation ($\Delta G^{\ddagger}$ in kcal mol^{-1}) for various conformational processes in **2–5**. Values reported are means ($\pm$0.15 kcal mol^{-1}) of results over the temperature ranges (°C) given in parentheses

Compound	N inversion [^{1}H; 400 MHz]	N–Bu^t rotation [^{13}C; 75.5 MHz]	N–Ad rotation [^{13}C; 75.5 MHz]	N–Et rotation [^{13}C; 75.5 MHz]
Bu^{t}CH$_2$N(Bu^t)CH$_2$CH$_3$ **2**	8.1_5 (−94, −101)	7.3 (−97, −118)		6.0 (−138, −141)
Bu^{t}CH$_2$N(Ad)CH$_2$CH$_3$ **3**	8.2_5 (−89, −94)		7.6 (−94, −114)	
AdCH$_2$N(Bu^t)CH$_2$CH$_3$ **4**	8.8_5 (−85, −105)	7.5 (−94, −105)		
Bu^{t}CH$_2$N(Bu^t)CH$_2$-Pr^i **5**	8.1 (−94, −99) [^{13}C, 75.5 MHz] 8.4_5 (−95, −99)	7.2 (−123)		

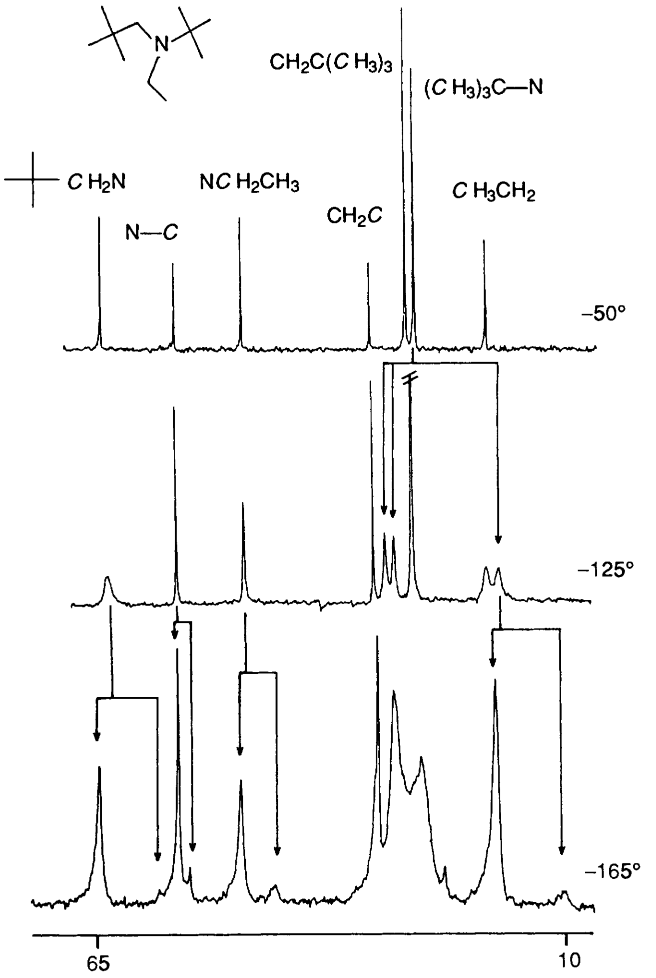
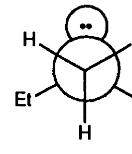


Fig. 1 ^{13}C NMR spectrum (75.5 MHz) of **2** in CHF$_2$Cl at various temperatures. The single methyl signal at −50 °C for the *N*-Bu^t group splits as shown into three equally intense signals at −125 °C owing to restricted N–Bu^t rotation. Below −150 °C the majority of lines are split into pairs of signals (ratio 9:1) from different rotational conformers owing to restricted N–Et rotation.



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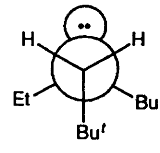

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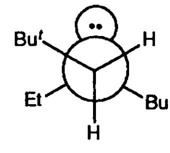

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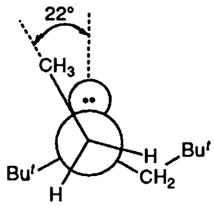

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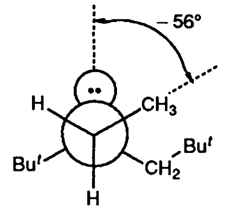

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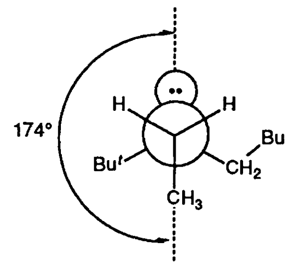

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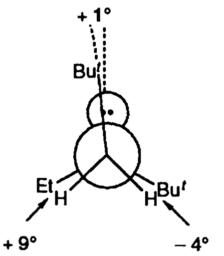

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between two unequally populated conformations presumably involving rotational conformations of the ethyl group.

For compounds **3–5**, the barriers to nitrogen inversion-rotation and to *N*-*tert*-alkyl rotation could be measured from spectral changes similar to those reported for **2**, see Table 4. Further broadening of ethyl- or isobutyl-group signals was observed at very low temperatures, analogous to that reported for **2**, but crystallisation took place before the signals had split. It is reasonable to believe that for **3** and **4** ethyl-group rotational barriers comparable to that for **2** are obtained, as is a similar sized barrier for isobutyl-group rotation in **5**.

A detailed molecular mechanics investigation of **2** was carried out using Allinger's MM282 program,[17] but only curtailed results need be reported here since conformations like **9** and **10** with *tert*-butyl groups *gauche* to each other are at least 6.5 and 8.5 kcal mol^{-1} less stable then *anti*-conformations like **11**. For this latter conformation type, there is a set of three ethyl-group conformations depending on the position of its methyl group with respect to the lone pair, +*gauche*, **12**; −*gauche*, **13**, and *anti*, **14**, whose calculated structures are described in Table 5.*

There exists a second set of mirror-image conformations **12′–14′** not shown which interconverts with the first set by the nitrogen inversion–rotation process. Rotation about the nitrogen–ethyl bond effects interconversions within each set.

On the basis of the calculations and assuming identical entropies for the different conformations, **2** should exist as a

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* Two different minimum-energy forms of each of **12–14** exist as a result of the methyl group being rotated to one or other side of the perfect staggering to reduce parallel 1,3-interactions. The results in Table 2 are for the more stable minima for **12–14**. The second minimum of +*gauche* **12** is not untypical in having a dihedral angle of 62° rather than 22° and being more than 3 kcal mol^{-1} less stable. The potential-energy diagram for ethyl-group rotation does not show these other staggered conformations because they are not encountered in the dihedral drive process without minimisation.

Table 5 Molecular mechanics calculations for the three most stable ethyl group conformations in *N*-ethyl-*N*-*tert*-butylneopentylamine, **2**

Conformation	$12+g+g$	$13+g+g$	$14+g+a$
E_{rel}/kcal mol^{-1}	0.0[a]	1.20	0.67
Dihedral angles/°			
Bu^t–CH$_2$–N–lp	+26	+1	+9
CH$_3$–CH$_2$–N–lp	+22	−56	+175
Bu^t–N–CH$_2$–Bu^t	+142	+119	+132
Δ(CH$_3$–C$_q$–N–lp)	9.1	2.6	11.0
Bond Angles/°			
Et–N–Bu^t	114.1	110.6	115.4
Et–N–CH$_2$–Bu^t	110.6	111.1	111.5
Et–N–lp	106.3	107.1	104.9
Bu^t–N–CH$_2$–Bu^t	112.9	113.9	114.4
Bu^t–N–lp	106.0	107.0	104.4
Bu^{t}CH$_2$–N–lp	106.4	107.0	104.9
Strain (E_s/kcal mol^{-1})			
Compression	2.56	3.08	2.49
Bending	5.24	6.06	7.26
Stretch bend	0.70	0.82	0.79
Van der Waals 1, 4	9.01	8.94	8.56
Van der Waals other	−0.89	0.40	−0.68
Torsional	8.89	7.42	7.75

[a] The final steric energy of Allinger's MM282 Program[17] is 25.51 kcal mol^{-1}. [b] The mean of the arithmetical values of the difference between the dihedral angle calculated and perfectly staggered values *viz.* 60 or 180°.

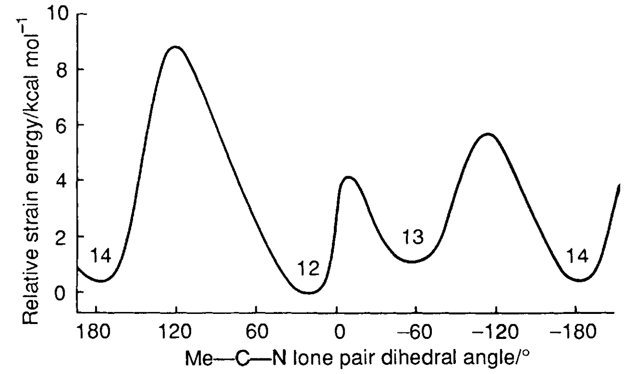

Fig. 2 Calculated (MM2) potential-energy diagram for rotation about the N–ethyl bond in **1**

mixture comprising 95.2, 0.4 and 4.4% of **12**–**14** and their enantiomers, respectively, at −165 °C, while at 25 °C these percentages are 64.9, 8.6 and 26.5, respectively.

The −*gauche* conformation, represented as **13**, is unusual in that the Newman projection along the N–CH$_2$ bond of the neopentyl group has all groups eclipsed, see **15**. We have observed and explained similar behaviour for a neopentyl group before.[1,12,18] The conformation, **15**, is also non-alternating, with the H–C–H projection inside the Et–C–Bu^t projection, but this is an almost inevitable accompaniment to such eclipsing.[18] Here, though not in other cases,[18] this unusual conformation is only the third most likely one, populated to only 8.6% even at room temperature according to calculations.

As emerged in the study of the benzyl equivalent of these ethyl compounds,[11] the dominant conformational effect is the preference for the two *tert*-alkyl groups to be *anti* to each other along the N–CH$_2$ bond, for the relative energies of conformations **12**–**14** inversely reflect the Bu^t–N–CH$_2$–Bu^t dihedral angle. What these dihedral angles do reflect directly is the differing perturbation introduced by the ethyl substituent in its three different conformations, **12**–**14**. The relative instability of conformation **13** is not due to the eclipsed neopentyl group, because the total of the torsional plus the van der Waals 1,4-strain for that conformation is lower than that for the more stable **12** and **14**, but is due rather to longer-range interactions between the *tert*-butyl groups which are now quite far removed from being *anti* to each other. The calculations suggest that in **13** the two largest hydrogen–hydrogen repulsions between the *tert*-butyl groups, although they are 1,8-interactions, are alone worth 0.63 kcal mol^{-1}.

Using the dihedral drive option in the MM282 molecular-mechanics program, the potential-energy diagram for ethyl-group rotation was calculated and is shown in Fig. 2. The relationship between the conformations **12**–**14** emerges clearly, and the dynamic process observed to become slow on the NMR timescale is the interconversion of **12** and **14** by way of **13** and a transition state which corresponds to the methyl group eclipsing the neopentyl group. The good agreement of this experimental barrier of 6.0 kcal mol^{-1} with the calculation of 5.7 kcal mol^{-1} is quite expected for rotation about carbon–nitrogen bonds[6,14] and contrasts with relatively poor agreement of calculation and experiment for carbon–carbon bonds.[19–21]

The nature of the changes in the proton NMR spectra at low temperature can reasonably be taken to confirm the conformational picture suggested by calculations. Thus the two multiplets observed for the methylene protons of the ethyl group at −100 °C when nitrogen inversion is slow have a large relative chemical shift of 0.68 ppm. This suggests[22] that one methylene proton is predominantly *anti* to the lone pair, and the other one is *gauche*, in agreement with a conformational mixture which is predominantly **12**. On further cooling the *anti* proton signal changes dramatically while the *gauche* signal does not. This agrees with the slowing of the **12**–**14** equilibrium, for the *anti*-proton in **12** becomes a *gauche* proton in **14**, with a large change in chemical shift, while the −*gauche* proton in **12** retains a similar chemical shift as a +*gauche* proton in **14**.

The ethyl-group rotation barrier in **2**–**4** is not significantly greater than that in simple ethylamines, confirming once again that increasing steric congestion need not lead to larger differences between the rotational ground and transition states, *i.e.* barriers. There is no reason to expect, however, that ethyl-group rotational barriers in the equivalent hydrocarbons, *e.g.* Bu^{t}CH$_2$CH(Bu^t)Et are as large as for **2**–**4**.

The rotational barriers of *ca.* 7.3 kcal mol^{-1} for the N-*tert*-alkyl bonds in **2**–**5** are probably smaller than those to be expected for the corresponding hydrocarbons, for neopentyl substituents are known[11] to raise such hydrocarbon barriers. Once again ground-state congestion seems to be important.

The nitrogen inversion–rotation barriers of 7.9 kcal mol^{-1} are smaller than those of *ca.* 9.2 kcal mol^{-1} found in analogues with a benzyl instead of an ethyl group,[12] but larger than in similar amines without the *C*-*tert*-butyl group, for in *N*-methyl-*N*-ethyl-*tert*-butylamine,[6] **2** without the *C*-*tert*-butyl group, the nitrogen inversion barrier is 7.2 kcal mol^{-1}. In *N*-neopentyl-*tert*-butylamines, interconversion of configurations like **6** and **7** requires not only passage through a structure flat at nitrogen, but also 180° rotation about the *N*-neopentyl bond. The two processes need not occur simultaneously for that would make the activation energy unnecessarily large, but since the rotation involves the *C*-*tert*-butyl group eclipsing the third *N*-substituent or the *N*-*tert*-butyl group it undoubtedly contributes somewhat to the measured barrier. We use the term nitrogen inversion–rotation since it serves no purpose to ignore the need for substantial rotation of substituents as well as flattening at the nitrogen centre.

Experimental

Dynamic NMR procedures and molecular mechanics calculations have been described previously.[12]

The synthesis of tertiary alkylamines **2**–**5** from known[12] secondary amines by way of the *N*-acetyl or *N*-isobutyroyl derivative followed a general method which is now described in detail for **2**.

N-*Ethyl*-N-tert-*butylneopentylamine* **2**.—*N*-*tert*-Butyl-*N*-neopentylacetamide (**16**); (19 g, 10 mmol) was added to $LiAlH_4$ (0.6 g, 15.4 mmol) suspended in a 1 : 2 mixture of ether and di-n-butyl ether. Reduction was complete (GLC) after 3 h at 105 °C. The mixture was cooled to 10 °C and 20 cm^3 of water were added dropwise, controlling the exothermic reaction. The precipitate was filtered off and the organic layer was dried with anhydrous sodium sulphate and the solvent was removed under reduced pressure. The crude product was distilled to yield the pure amine (1.5 g, 88%) b.p.$_{760}$ = 152–155 °C (Found: M^+ 171.199 20. Calc. for $C_{11}H_{25}N$: *M*, 171.198 699; Δ 1.8 ppm).

N-*Ethyl*-N-(1-*adamantyl*)*neopentylamine*, **3**. (Found: M^+ 249.245 78. Calc. for $C_{17}H_{31}N$: *M*, 249.245 649; Δ 0.5 ppm).

N-*Ethyl*-N-(1-*adamantylmethyl*)-tert-*butylamine*, **4**. (Found: M^+ 249.244 80. Calc. for $C_{17}H_{31}N$: M^+ 249.245 649; Δ 3.4 ppm).

N-(1-*Isobutyl*)-N-tert-*butylneopentylamine*, **5**. (Found: M^+ 199.229 63. Calc. for $C_{13}H_{29}N$: *M*, 199.229 999; Δ 2.9 ppm).

NMR spectra of compounds **2**–**5** are described in Tables 2 (^1H) and 3 (^{13}C).

N-tert-*Butyl*-N-*neopentylacetamide* **16**.—To a solution of *N*-*tert*-butylneopentylamine[12] (7.15 g, 50 mmol) and triethylamine (6.06 g, 60 mmol) in chloroform was added pivaloyl chloride (5.43 g, 45 mmol), keeping the temperature below 30 °C with cooling. The mixture was refluxed for 4 h, cooled to 25 °C and water (25 cm^3) was added. The organic layer was washed with water, dried and the solvent was removed under reduced pressure to obtain crude amide (6.3 g, 76%) which was used without further purification. δ($CDCl_3$; 200 MHz) 0.90 (9 H, s, CMe_3), 1.40 (9 H, s, $NCMe_3$), 2.10 (3 H, s, CMe) and 3.3 (2 H, s, C*H*$_2$). δ_C($CDCl_3$; 50 MHz) 25.8 (1 C, Me), 29.3 (3 C, $CCMe_3$), 29.5 (3 C, NC*Me*), 32.9 (1 C, *C*Me$_3$), 55.5 (1 C, CH_2), 57.3 (1 C, N*C*Me$_3$) and 177.7 (1 C, CO).

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