Chemical shifts of the protons within a methyl group in a saturated hydrocarbon. Slow methyl group rotation

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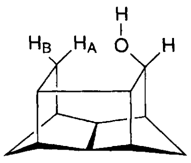
In the proton NMR spectrum of both $(Bu^t)_3CH$ and $(Bu^t)_3COH$ at −150 °C, one of the three separate signals for the methyl groups of a *tert*-butyl group appears as three singlets of equal intensity, with a greater than 1 ppm range of chemical shifts, showing that one methyl group is rotating slowly on the NMR timescale with a barrier to 120° rotation of 5.3 kcal mol^{-1} (1 cal = 4.184 J).

The rationalisation and calculation of proton chemical shifts for simple organic molecules is of recurring interest.[1,2] This paper reports a saturated acyclic hydrocarbon where rotation of one kind of methyl group is slow on the NMR timescale at low temperature with the three individual proton chemical shifts within the methyl group ranging over more than 1 ppm.



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One of the principal difficulties in understanding proton shifts is the unsatisfactory nature of the experimental evidence beyond that from some rigid relatively unstrained bicyclic molecules. With less rigid saturated hydrocarbons, most methyl, methylene and methine groups chemical shifts (ignoring solution effects) reflect an average of up to three different staggered conformations, and may also be susceptible to conformational averaging of more distant alkyl substituents.

Even if the conformation of each bond in a molecule is known, an additional factor, steric compression, plays a significant role.[3] The classic demonstration of this[3] is the bridged compound **1** where the compressed proton H_A appears uncommonly downfield (δ = 3.55), but also, the uncompressed proton H_B is at compensatingly high field (δ = 0.88), implying a redistribution charge and thus of electronic shielding over the CH_2 group.

The subject of this communication is $(Bu^t)_3CH$ **2**[4,5] but it is useful to discuss the corresponding alcohol $(Bu^t)_3COH$ **3**[6–8] as well. In both **2** and **3**, rotation of one kind of methyl group is slow on the NMR timescale below about −145 °C, the proton NMR of the *tert*-butyl groups appearing as five singlets of relative intensities 1 : 1 : 1 : 3 : 3 at −157 °C. There is much

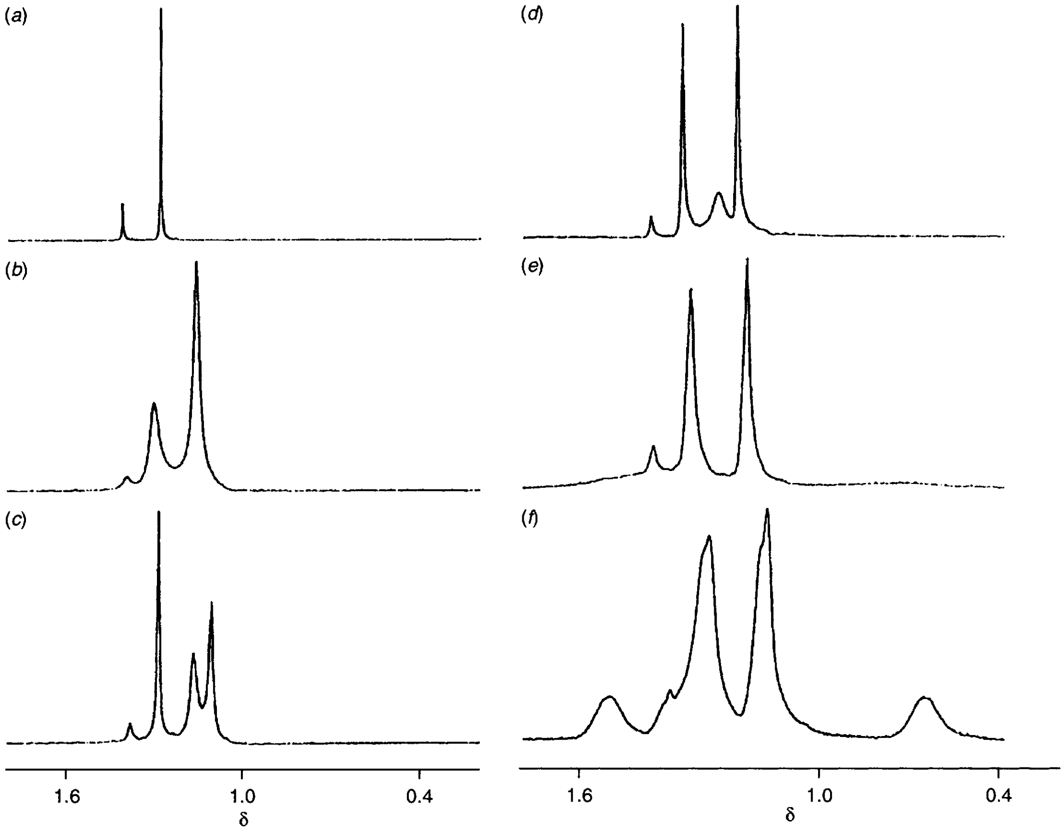


Fig. 1 Proton NMR of **3** at (*a*) 20, (*b*) −86, (*c*) −111, (*d*) −125, (*e*) −145, (*f*) −157 °C

overlap of these peaks for **2** see Table 1, so the spectrum for **3** is illustrated in Fig. 1.

The three methyl groups of any *tert*-butyl group are non-equivalent and at −157 °C two give signals which are intense singlets at δ 1.17 and 1.36 while the third methyl group gives three singlets each of one-third intensity at δ 0.63, 1.48 and 1.68, a chemical shift range of 1.05 ppm. These three singlets should be 1 : 2 : 1 triplets due to mutual geminal coupling but this is obscured by low temperature broadening. The OH proton occurs at δ 1.30 (see Table 1).

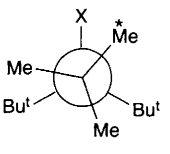
This spectrum is the culmination of three sets of changes in the *tert*-butyl proton signal as the temperature is lowered, two of which have been described previously.[7,8] At room temperature the proton NMR spectrum of **3** at 400 MHz shows two singlets of relative intensity 27 : 1. On cooling the *tert*-butyl singlet broadens and splits to a 2 : 1 doublet below about −60 °C [see Fig. 1(*b*)] since rotation through the eclipsed transition state (**4** to **5**) has become slow on the NMR timescale.[7] At lower temperatures this splits to a three singlets of equal intensity but different width [see Fig. 1(*c*)] as libration through the staggered transition state (**4** to **6**) becomes slow on the NMR timescale. During 360° of rotation there are thus six sites of three different types, A, B or C, which a methyl group may occupy (see **7**), hence the three NMR signals. Corresponding changes are seen in the ^{13}C NMR spectra, and have also been outlined[5] for compound **2**, see Table 1 for spectra and Table 2 for barriers.

Further cooling produces no changes in the ^{13}C NMR, but in the ^{1}H NMR leads to the broadening and eventual splitting of the middle of the three methyl singlet signals for **3** to give the three widely spaced singlets of equal intensity described above [see Fig. 1(*d*–*f*)]. The three protons of one of the methyl groups are different on the NMR timescale, and from the spectral changes, a barrier of 5.3 kcal mol^{-1} for methyl group rotation is derived. In contrast to the usual situation[9] where three isotopically different hydrogen atoms in a methyl group make a molecule chiral, a chiral conformation like **10** makes three isotopically identical hydrogen atoms different. The proton NMR of **2** shows similar changes except that at lowest temperatures, signals of the two faster-rotating methyl groups and one further proton overlap.

Table 1 ^{1}H^{a} and ^{13}C^{b} chemical shifts of **2** and **3** at various temperatures

	δ (*T*/°C)	
^{1}H NMR	**2**	**3**
$HC(Bu^{t})_3$	1.505 (20) 1.280 (−157)	
$[(CH_3)_3C]_3$	1.345 (20)	1.388 (20)
	0.63, 1.14, 1.25, 1.67 (−157)	0.63, 1.17, 1.36, 1.48, 1.68 (−157)
	[1 : 6 : 1 : 1]^{c}	[1 : 3 : 3 : 1 :]^{c}
^{13}C NMR		
$HC(Bu^{t})_3$	66.13 (20)	69.80 (20)
$HC[C(CH_3)_3]_3$	39.50 (20), 38.29 (−145)	46.35 (20), 46.10 (−145)
$HC[C(CH_3)_3]_3$	35.56 (20)	33.28 (20)
	26.50, 38.48 (−112)	29.34, 34.67 (−60)
	[1 : 2]^{c}	[1 : 2]^{c}
	25.74, 37.93, 38.69 (−135)	29.10, 32.44, 37.53 (−85)
	[1 : 1 : 1]^{c}	[1 : 1 : 1]^{c}

^{a} Relative to $CHDCl_2$, δ 5.32. ^{b} Relative to CD_2Cl_2, δ 53.8. ^{c} Relative intensities.



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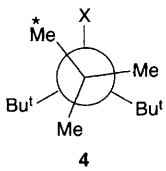

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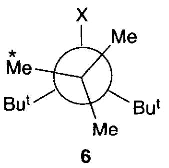

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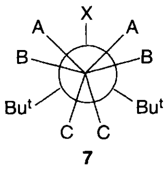

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Only two earlier reports of slow methyl group rotation on the NMR timescale are known in the forty year history of dynamic NMR spectroscopy.[10] In both, a range of 9-methyl-triptycenes[11–13] like **8** and 1-fluoro-8-*tert*-butylnaphthalene **9**,[14] the methyl group has to rotate against a rigid aromatic framework. This is undoubtedly the origin of the high barriers to rotation, $\Delta G^{\#}_{150\,\mathrm{K}}$ = 7.2–12.0 for members of series **8** and 6.9 kcal mol^{-1} for compound **9**.

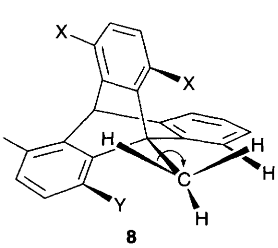
Molecular mechanics calculations were carried out for both **2** and **3** using Allinger's MM3 program,[15] and gave equivalent minimum energy conformations with all three *tert*-butyl groups skewed in the same direction as in **4** or **5**. Using the dihedral drive option in the MM3 program, barriers to rotation and libration of the *tert*-butyl group and to rotation of a methyl group in environments A, B. C (see **7**) were calculated, as shown with the experimental results in Table 2. Since the calculated rotation barrier for methyl group B is much greater than for groups A and C, the experimental barrier of about 5.3 kcal mol^{-1} is assigned to rotation of methyl group B, see **7**. The calculations suggest that there are no distortions that are unusual for methyl groups B compared with groups A and C, and agree satisfactorily with the electron diffraction-derived experimental parameters[16] for the alkane **3** and earlier molecular mechanics calculations.[17]

The agreement with experiment of the calculated methyl and *tert*-butyl group rotation and libration barriers shown in Table 1 is less good, although trends are correct. This probably reflects the difference between the simplicity of the dihedral drive simulation and the more-or-less correlated nature of these processes in practice.[18]

The simplified diagram **10** which is based on the calculated structure suggests the origin of the high rotation barrier for methyl group B. Two hydrogens of that group are enclosed between methyl groups A and C of the adjacent *tert*-butyl group, and significant movement of the *tert*-butyl group which is in a steep-sided rotational potential energy well[7] must accompany rotation of methyl group B. In keeping with this picture and the known fact that steric compression produces downfield chemical shifts,[3] two of the protons of methyl group B appear markedly downfield from the third.

For all three rotation processes in **3**, the barrier heights in solution are lower than found in the solid state.[8,10] This agrees with other recent examples[19] and suggests that in the solid even the methyl group is aware of the lattice.

Slow methyl group rotation on the NMR timescale for **2** and **3** means that there is no significant conformational averaging



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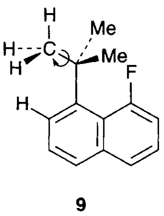

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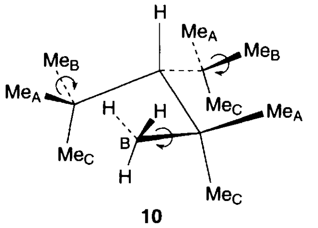
Table 2 Dynamic NMR barriers $\Delta G^{\#}$ (and MM3 calculated barriers $\Delta H^{\#}$) to libration and rotation processes

	Me Group		Bu^t Group			
	Rotation		Libration		Rotation	
Compound	$\Delta G^{\#}_{exp}$/ kcal mol^{-1} (T/°C)	$\Delta H^{\#}_{calc}$/ kcal mol^{-1}	$\Delta G^{\#}_{exp}$/ kcal mol^{-1} (T/°C)	$\Delta H^{\#}_{calc}$/ kcal mol^{-1}	$\Delta G^{\#}_{exp}$/ kcal mol^{-1} (T/°C)	$\Delta H^{\#}_{calc}$/ kcal mol^{-1}
2	5.2 (−143)	7.4 3.1 2.1	6.5 (−120)	8.0	6.8 (−120)	9.4
3	5.3 (−150)	7.7 3.4 0.7	9.2 (−80)[a]	9.0	10.0 (−60)[a]	10.3

[a] See ref. 9.



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for the three protons since all other large-amplitude internal motion except rotation of the symmetrical methyl groups A and C is slow. The remarkable 1.04–1.05 ppm range for chemical shifts within one methyl group is the result. Not only are there two sterically compressed protons deshielded, but there is complementary shielding of the remaining proton δ = 0.63, supporting the suggestion[3] that steric compression produces a polarisation of electron distribution within the group. The average chemical shift of the three protons in B is very similar to that of the rotationally averaged methyl groups A and C.

Conformational motions thus mask quite dramatic ranges in individual proton chemical shifts even in a saturated hydrocarbon, a point already noted from a tabulation[20] of methine proton chemical shifts in the twenty saturated acyclic hydrocarbons $HCR^1R^2R^3$ (R = Me, Et, Pr^i, Bu^t). Such individual proton chemical shift values in saturated hydrocarbons are the data that any one calculating proton chemical shifts is challenged to match.

Methyl group rotation appears to be slow on the NMR timescale also in both $R(Bu^t)_2COH$ and R_2Bu^tCOH (R = adamantyl), but adamantyl group proton NMR signals obscure the significant changes in the spectrum.

I am grateful to Dr J. S. Lomas for a generous sample of tri-*tert*-butyl carbinol, and to Mr C. J. Cooksey for transforming it into the alkane.

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Received, 28th July 1995; Com. 5/05012J