Hindered Rotation in a 1-Alkylnaphthalene. A Dynamic Nuclear Magnetic Resonance, Difference Nuclear Overhauser Enhancement, and Molecular Mechanics Investigation of 1-Neopentylnaphthalene. The t-Butyl Group as a Probe of Chirality

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A consideration of earlier results suggests that in contrast to other simple 1-alkylnaphthalenes, the barrier to rotation of the neopentyl group in 1-neopentylnaphthalene may be high enough to be measured by dynamic n.m.r. spectroscopy. A synthesis is reported, and changes in the n.m.r. spectrum at low temperature suggest a barrier to rotation of 5.15 kcal mol^{-1}. Molecular mechanics calculations and difference NOE n.m.r. experiments suggest the structure of the ground state and transition state conformations, and the latter is not, apparently, the one with the t-butyl group in the plane of the naphthalene ring. The barrier to rotation of the naphthyl group in the much more highly substituted 2-t-butyl-2-(1-naphthyl)-1,3-dioxolane is only 5.15 kcal mol^{-1} as shown by two methyls of the slowly rotating t-butyl group becoming diastereotopic as rotation of the naphthyl group also becomes slow.

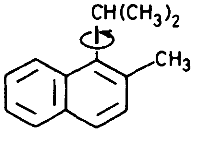
There have been many reports in the last few years of hindered rotation of the *peri*-substituent in *peri*-substituted naphthalenes.[1–8,†] Dynamic n.m.r. has been the most useful technique for recent studies but in fact substituted binaphthyls, which fall into this class, were first reported by Kuhn and Albrecht as long ago as 1929[5] and have been much studied since.[6] The barrier to rotation in a simple 1-alkylnaphthalene, however, has never apparently been recorded[7] and some reasons why can be gathered from a consideration of the examples of other *peri*-substituted naphthalenes for which barriers are known. These fall into three groups.

First there are 1-substituted naphthalenes with a substituent in the 2-position, *i.e.* *ortho*-substituted[2] such as (**1**).[2a] These need not be considered further, since the *ortho*-substituent no doubt has as much to do with the barrier as the unique environment of the *peri*-position.

The second group is the 1,8-disubstituted naphthalenes.[1,3,5,6] In general, barriers are high when the two substituents are planar *e.g.* (**2**),[1b] they are of intermediate size when one substituent is planar and one is tetrahedral, *e.g.* (**3**),[3b] and the rotational barrier is low when both substituents are tetrahedral, *e.g.* (**4**).[3a,b,d] Planar substituents can adopt stable ground states with few interactions, *e.g.* (**5**) for (**2**). In contrast, tetrahedral substituents interfere drastically with each other so that any ground state is destabilised; further, interconverting ground states may be structurally close one to another as in (**4**), which involves a six-fold barrier.

The third group comprises 1-substituted naphthalenes without further 8- or 2-substituents.[1,4] There are high barriers when the 1-substituent is planar, *e.g.* (**6**)[6a] or (**7**),[4e] but no examples[7] when the substituent is a simple tetrahedral one. The high barriers reflect again a stable, more or less orthogonal ground state (**8**) (φ *ca.* 90°), and strong interference in the rotational transition state, *e.g.* (**9**).

These results suggest what kind of simple alkyl group is most likely to show a measurable barrier to rotation. Clearly there must be two equivalent stable conformations separated for preference by 180° of rotation (*i.e.* a two-fold barrier rather than say a six-fold barrier such as might obtain in 1-t-butylnaphthalene). Further, while there should be a sterically demanding substituent to interfere with the naphthalene ring during rotation, this substitution should be chosen to allow a ground state as free from strain as possible. While this may seem very obvious, it is worth emphasizing since highly strained molecules have failed to give measurable barriers.[3b] A last point is that the substituent should be such that its n.m.r. spectrum will show changes when rotation is slow on the n.m.r. timescale.



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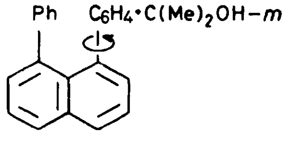
ΔG‡ *ca* 113 kcal mol^{-1}



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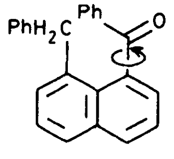
ΔG‡ 17·3 kcal mol^{-1}



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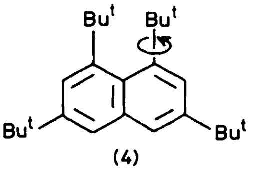
ΔG‡ 11·9 kcal mol^{-1}



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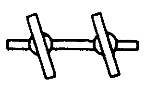
ΔG‡ 6·5 kcal mol^{-1}



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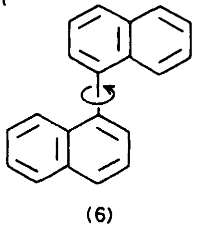

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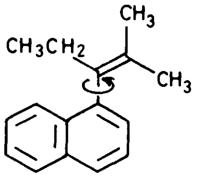
† Proton [9a,b] and carbon-13[9c] n.m.r. relaxation time measurements have been interpreted in terms of the barrier to rotation of methyl groups in 1-methylnaphthalene[9a,c] and 1,8-dimethylnaphthalene[9b] of *ca.* 2.2 and 3.0 kcal mol^{-1}, respectively.



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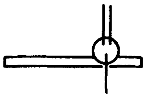

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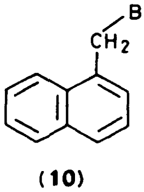

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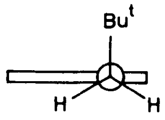

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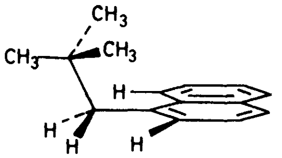

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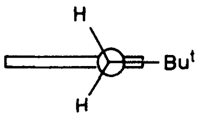

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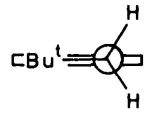

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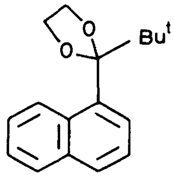

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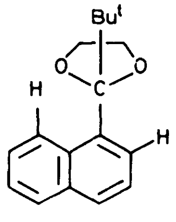

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For these reasons we chose to study 1-neopentylnaphthalene (**10**). The ground-state conformation is likely to be close to the one shown from different viewpoints in (**11**) and (**12**). Rotation through 180° about the naphthyl–CH_2 bond interconverts enantiomeric conformations, by way of obviously strained structures where that butyl group is near to the plane of the naphthalene ring *e.g.* (**13**), and even more so for (**14**). The precise conformation of the ground state will be discussed later.

Once we had examined 1-neopentylnaphthalene, and as a further consequence of the analysis we have given above, we prepared and examined a more highly substituted analogue, (**15**), the ethylene glycol acetal of 1-naphthyl t-butyl ketone, 2-t-butyl-2-(1-naphthyl)-1,3-dioxolane. We did not expect to find a much higher barrier in this more highly substituted compound since the additional substituents will particularly affect the ground-state conformation, the oxygens interacting with 8-H and 2-H as in (**16**). We obtained further information about the ground state of (**10**) from measurements of proton relaxation times, of proton–proton nuclear Overhauser effects, and from molecular mechanics calculations.

Results

(a) *Dynamic N.m.r.*—The 200 MHz ^1H n.m.r. spectrum of (**10**) comprises a complex aromatic region, and otherwise two singlets of intensity ratio 1:4.5 at δ 3.04 and at δ 0.97 assigned to the CH_2 and the t-butyl groups, respectively. On lowering the temperature, there is no significant change down to *ca.* −140 °C when the CH_2 signal begins to broaden relative to the t-butyl signal and below *ca.* −156 °C it splits and appears at −161 °C as a broad doublet at δ 2.70 and 3.38. Assuming that this would appear as an AB quartet if sufficient resolution at a sufficiently low temperature were obtained,† the rate of rotation of the neopentyl group at the coalescence temperature of −156 °C is *ca.* 300 s^{-1} and thence the barrier to rotation of the neopentyl group is 5.3 kcal mol^{-1}. This assumes a transmission coefficient of 1.0 for the rotation. With a transmission coefficient of 0.5 the barrier is 0.15 kcal mol^{-1} lower (see Discussion section). At even lower temperatures there is additional broadening of the t-butyl signal compared with the CH_2 signals which may be associated with t-butyl rotation becoming slow on the n.m.r. timescale with a barrier somewhat <5 kcal mol^{-1}. This is not unequivocal from the spectrum, but analogies for such a rotation *within* a neopentyl group do exist.[10a]

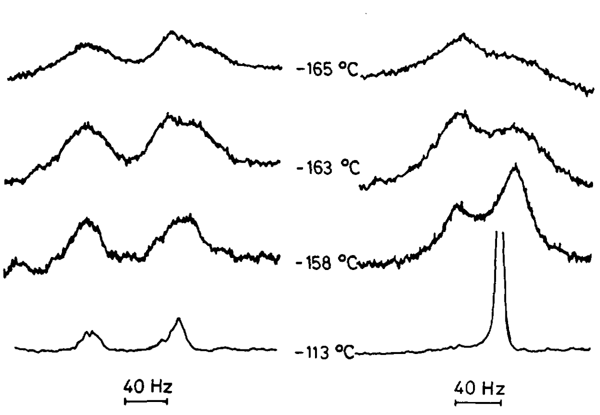

Figure 1. 200 MHz ^1H N.m.r. spectra of the OCH_2CH_2O and t-butyl groups of the compound (**15**) at various temperatures.

The n.m.r. spectrum of (**15**) showed, apart from a complex aromatic region, a multiplet apparently of the AA′BB′ type at δ 3.68 and 3.94 for the OCH_2CH_2O group and a singlet at δ 1.02 for the t-butyl group. On cooling below −148 °C, the t-butyl group showed changes which could be related to rotation about the β-bond. The t-butyl signal appeared as a 1:2 doublet at −158 °C, at δ 0.90 and 1.15 and, from the coalescence at −153 °C, the barrier to rotation of the t-butyl group is calculated to be 5.7 kcal mol^{-1}.

Below *ca.* −158 °C, the OCH_2CH_2O signals broaden, as does the upfield, more intense part of the 1:2 t-butyl doublet, and at *ca.* −168 °C, the upfield part of the OCH_2CH_2O signal is clearly two broad signals, and the t-butyl signal is now apparently a 2:1 doublet (see Figure 1). The precise chemical shifts involved are clearly difficult to measure precisely but agree with a rate constant for rotation of the naphthyl group of *ca.* 85 at *ca.* −163 °C which corresponds to a barrier to rotation of 5.3 kcal mol^{-1}. If a transmission coefficient of 0.5 is assumed, the barrier is 0.15 kcal mol^{-1} lower.

(b) *Proton–Proton Difference NOE Spectroscopy.*—Irradiation in successive experiments at several positions in the ^1H n.m.r. spectrum of (**10**) produces small proton–proton nuclear Overhauser effects which can be demonstrated by difference techniques,[10b] *i.e.* by repeatedly recording spectra with and without double irradiation, and subtracting these to obtain a difference spectrum containing only the nuclear Overhauser

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† The methylene hydrogens can be assumed to have a coupling constant of 13.5 Hz, the value found for some hindered neopentylbenzenes.[9]

Table. Proton–proton nuclear Overhauser enhancements observed in 1-neopentylnaphthalene (**10**)

When the protons indicated below are irradiated	The size (%) of the nuclear Overhauser effects observed at the various positions are				
	Ring H-2	Ring H-8	α-CH$_2$	Methyl of Bu^t	Other
Methyl of t-butyl	+5.0	+2.9	+2.6		
α-CH$_2$ group	+8.4	+11.4		+0.9	Ring H-3 or H-7, −2.9
Ring H-2			+0.8	+0.5	
Ring H-8			+2.0	+0.2	Ring H-7 +4.6

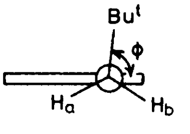
enhancement not in the normal spectrum. Accumulation of a number of these difference spectra allows the enhancement to be better distinguished from noise. The results are shown in the Table.

On irradiation at the t-butyl signal, most of the aromatic protons, which are not relaxed by the t-butyl group, do not therefore appear in the difference spectrum. The methylene group, the proton in the 2-position, and the proton in the 8-position are relaxed in part by the t-butyl group, and nuclear Overhauser enhancements are detected in the difference spectrum. The magnitude of the effect of irradiation at the t-butyl group is greater at the 2- than at the 8-position. Irradiation at the CH$_2$ position has a greater effect on the 8- than on the 2-position. Irradiation at the aromatic hydrogens has only small effects on the side-chain hydrogens, but irradiation at the 2-position does have a greater effect on the t-butyl signal than does irradiation at the 8-position, while the reverse holds for the CH$_2$ signal.

The absolute magnitude of NOEs observed at the CH$_2$ and t-butyl signals is smaller than that on the aromatic signals because the former have relaxation pathways other than by dipole–dipole interaction with the irradiated hydrogens.

The conclusion to be drawn from the NOE experiments is that 1-neopentylnaphthalene spends rather longer in the set of conformations like (**17**) (φ < 90°) than in the set of conformations like (**18**) (φ > 90°).

(c) *Relaxation Times.*—The spin-lattice relaxation times of the protons in the 2- and 8-position are quite different at 9.1 and 3.7 s, respectively. If we can assume that dipole–dipole interaction dominates spin-lattice relaxation of these protons, then since each has an *ortho*-hydrogen neighbour, the difference in relaxation times may reasonably be attributed to the substituent in the 1-position whose interactions are presumably greater with the 8- than with the 2-position. This last assumption is supported by the molecular mechanics studies discussed below which calculate that in the ground state the nearest approach of the t-butyl and methylene hydrogens to the 2-position is 2.60 and 3.67 Å, respectively, while for the 8-position the corresponding values are much less at 2.33 and 2.11 Å, respectively.



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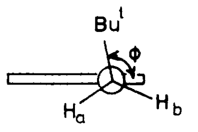

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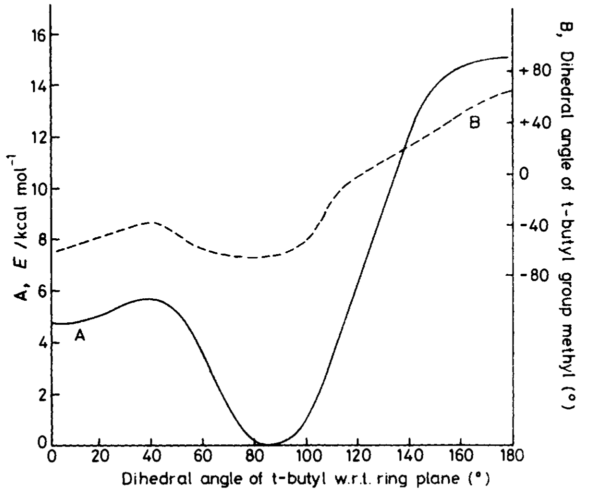


Figure 2. Variation of the steric energy of (**10**) (solid line) with rotation about the naphthyl–neopentyl bond. Variation of the dihedral angle of the methyl groups of (**10**) (broken line) with rotation about the naphthyl–neopentyl bond. These are results of calculations using the MM2 programme

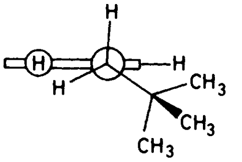
(d) *Molecular Mechanics Calculations.*—Using Allinger's programme MM2,[11] we have calculated the minimum-energy conformation of 1-neopentylnaphthalene. The following are the interesting characteristics. The t-butyl group is almost orthogonal to the ring but is slightly directed towards the 2-position as in (**17**) with φ 86.4°. There is calculated to be a small lengthening of carbon–carbon bonds compared with standard values, but this is quite unexceptional for a neopentyl group or a 1-substituted naphthalene. The bond angles at the α-carbon are quite different from the normal in a not unexpected way, with the naphthyl–C$_\alpha$–C$_{tert}$ angle opened up to 115.7°, while the H–C$_\alpha$–H angle is closed down to 103.1°.

The most important repulsive interaction of the neopentyl group with the naphthalene ring appears to be between the *peri*-H-8 and the methylene group hydrogen nearer to it [H$_a$ in (**17**)]. This is reflected by the H$_a$–C$_\alpha$–naphthyl bond angle of 110.7° compared with 108.0° for H$_b$–C$_\alpha$–naphthyl.

Of the three methyl groups of the t-butyl group, the two which are gauche to the naphthyl group show small distortions of bond angles and dihedral angles due to their interactions with the naphthalene ring. The methyl next to the 8-position shows rather larger distortions than the one next to the 2-position.

A measure of the strain in the ground state comes from comparing the calculated steric energy of 1-neopentylnaphthalene, with a *peri*- and an *ortho*-interaction, with 2-neopentylnaphthalene, with two *ortho*-interactions. The latter appears to have the t-butyl group almost exactly orthogonal to the plane (φ 89.6°), and has 3.1 kcal mol^{-1} less steric energy than the former. As far as steric interactions are concerned, 2-neopentylnaphthalene should be equivalent to neopentylbenzene so 3.1 kcal mol^{-1} can be taken as the calculated value of the *peri*-strain of the neopentyl group in the ground state of (**10**). This additional strain in 1-neopentylnaphthalene is more than half the calculated and measured rotational barriers in that compound so ground state strain still seems to reduce the rotational barrier significantly.

By using the dihedral drive option in MM2 the dihedral angle φ was driven in steps of 10°, with smaller 1° steps around turning points, and the potential energy diagram for rotation of the neopentyl group shown in Figure 2 was calculated. These calculations suggest that interconversion of enantiomeric, near-to-orthogonal, ground-state conformations is achieved by rotation of the t-butyl past the 2-position, *i.e.* (**13**) with a barrier



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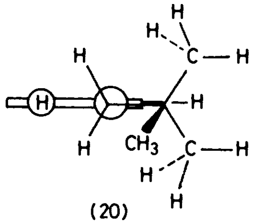

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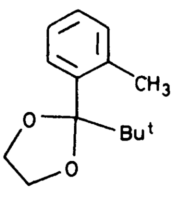

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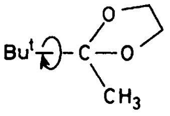

(22)

of 5.7 kcal mol^{-1}. Rotation of the t-butyl group past the 8-position, *i.e.* (**14**), has a barrier of 15.1 kcal mol^{-1} and is much more unlikely.

Discussion

Calculations and n.m.r. measurements combine to suggest that 1-neopentylnaphthalene exists as a rapid equilibrium of two relatively unstrained enantiomeric forms with the t-butyl group on one or other side of the plane and while near to orthogonal to the plane of the naphthalene ring, nonetheless slightly tilted towards the 2- rather than the 8-position. These two forms interconvert by rotation of the neopentyl group so that the t-butyl substituent passes through the plane of the ring, and the barrier to this rotation is measured as 5.15 kcal mol^{-1}.

The calculations show, as expected, that rotation of the t-butyl group past the 8-position is a particularly high-energy process which is unlikely to be the means of interconverting enantiomeric ground-state conformations (φ −87° and +87°). This is much more easily achieved by rotation of the t-butyl group past the 2-position, but the variation of the energy during this rotation is not straightforward.

The high-energy point on this interconversion is not where the t-butyl group is in the plane of the naphthalene (*i.e.* φ 0°) nor is it where one of the methylene hydrogens is in the plane with the hydrogen in the 8-position (*i.e.* φ 60°). Rather there are two enantiomeric high-energy structures intermediate between these two with φ 40 or −40°.

In this transition-state structure represented by (**19**), one of the methylene hydrogens is close to the hydrogen in the 8-position (but not the closest it ever is during rotation), and this interaction is calculated to contribute 0.65 kcal mol^{-1} to the barrier to rotation. The other striking interaction is that of the methyl group *anti* to this hydrogen, which has a marked interaction (calculated to be 1.3 kcal mol^{-1}) with the hydrogen in the 2-position of the naphthalene. This interaction has been reduced from an even higher value by a considerable rotation of the t-butyl group away from 60° dihedral angles with respect to the naphthyl-CH$_2$ group, which contributes 0.49 kcal mol^{-1} to the barrier. The other significant contributor to the barrier (1.25 kcal mol^{-1}) is calculated to be opening of the naphthyl–C–t-butyl bond angle.

There are of course many small changes in the contributions to the conformational energy during rotation, those we have mentioned being the most striking. A more detailed consideration of smaller contributions probably tells less about neopentylnaphthalene, and more about the parametrization of the programme.

That the t-butyl group rotates away from a 60° staggered conformation, to minimise long-range interactions encountered during rotation about the naphthalene–CH$_2$ bond, is quite reasonable, and the broken line in Figure 2 (which should be referred to the right-hand ordinate), shows the calculated average dihedral angle of the t-butyl methyl groups during the neopentyl rotation.

It is of equal interest that rotation in the other sense, with the t-butyl group passing the 8-position, also seems to require rotation about the CH$_2$–t-butyl bond away from perfect staggering. In fact, for φ 130°, the calculated minimum-energy conformation has the t-butyl group eclipsed with its two hydrogens and naphthalene neighbours! This eclipse makes chemical sense for it moves one of the t-butyl methyl groups through the plane of the naphthalene ring before the quaternary carbon of the t-butyl is in the plane *i.e.* before that particular methyl group gets very close to the *peri*-hydrogen in the 8-position.

In neopentylbenzene the barrier to rotation of the neopentyl group is reported[12a] to be less than 6 kcal mol^{-1}, and may very well be much less than this value. In any case dynamic n.m.r. studies did not afford a value for this barrier in three different compounds studied.[12a] That a barrier could be measured for (**10**) in this work even though the neopentyl group has been calculated to have 3.1 kcal mol^{-1} more steric energy than in neopentylbenzene is an indication that the *peri*-interaction provides a crucial enhancement of the barrier in the naphthyl compound. On this subject it is worth noting that the barrier to rotation in 1-methylnaphthalene is 2.2 kcal mol^{-1} [8a,c] whereas there is essentially no barrier to rotation in toluene.[8d] The metastable intermediate conformation with φ 0°, *i.e.* with the t-butyl in the plane, is calculated to be of slightly lower energy, partly because at this point perfect staggering of the t-butyl group with respect to the naphthyl–CH$_2$ bond also reduces interactions of the individual methyl groups with the 2-position [see (**20**)].

The existence of this intermediate metastable conformation between the two enantiomeric transition states means that the rate of interconversion of enantiomers will be only half the rate of surmounting the barrier represented by the transition state. That is to say, once the metastable state is reached, there is a 50% chance of returning to the initial state with no nett effect on the spectrum. The height of the barrier is then less than that implied by the measured rate of interconversion of conformations. This can be allowed for by introducing a transmission coefficient of 1/2 in the Eyring equation used to relate the rate of interconversion of conformations to the free energy of activation for rotation, *i.e.* the barrier. This leads to barriers 0.15 kcal mol^{-1} lower than reported in the Results section.

The barrier found for naphthalene rotation in (**15**) is not sensibly different from that in (**10**) in spite of the increased substitution. This bears out the proposition in the Introduction that strain in the ground state may produce low rotational barriers in this system. Such an explanation is supported by a comparison of (**15**) with (**21**),[12b] where the barrier to rotation (this time against the tolyl group) is as high as 11.7 kcal mol^{-1}. The naphthyl group might appear to be more hindering than the tolyl group, where the methyl substituent can no doubt be deformed, but it gives a much lower barrier, which we interpret as a further indication of ground-state strain in the naphthyl compound.

It is interesting that ground-state steric strain is also apparent in the rotational barrier *of the t-butyl group* in (**15**) and even in (**21**). The values of 5.7 and 6.3 kcal mol^{-1} are easily the lowest found for a t-butyl group attached to an *sp*^{3} carbon with three non-hydrogen substituents.[13] The nearest comparable value is, as it happens, for another acetal,[14] that of 7.5 kcal mol^{-1} for (**22**), quite markedly higher. We think the low barriers to t-butyl rotation in (**15**) and (**21**) may also be ascribed to ground-state strain of the t-butyl groups.[15]

That the t-butyl signal should change from a 1:2 doublet to an apparently 2:1 doublet, presumably a disguised 1:1:1 triplet, as the naphthyl rotation slows, is worthy of comment. Structure (**23**) is chiral when naphthyl rotation is slow, and the methyls of an R = isopropyl group, or the methylene hydrogens of an R = ethyl group, would be diastereotopic. In fact the groups X of any CX_2Y group would be diastereotopic. A t-butyl group is not apparently a 'CX_2Y group' and so cannot apparently be a probe of chirality in the sense of an isopropyl or an ethyl group. In (**15**) however, below −158 °C, t-butyl rotation is slow, and the t-butyl group takes on the form of a CX_2Y group. When, below −163 °C, naphthyl rotation is slow and the effects of a chiral conformation are seen, the X-part of the CX_2Y spectrum of the t-butyl group splits as the two X-methyl groups become diastereotopic. The only previous instance of a t-butyl group as a probe of chirality that we know of is that of tri-t-butylmethane and analogues studied by Mislow and Wroczynski.[16]

It is well known that the agreement between experimental values for barriers and those calculated by the MM2 programme is not particularly good, the calculated value being too low.[17] In the present case the reverse is found, the calculated barrier being 5.7 kcal mol^{-1} which represents quite good agreement with the experimental value of 5.1—5.3 kcal mol^{-1}. It is interesting that in a compound similar to (**10**), namely 1,3,6,-8-tetra-t-butylnaphthalene, comparatively good agreement was also found between experiment and calculation (**20**).[18]

It is perhaps tendentious to discuss agreement between a calculated enthalpy of activation and a measured free energy of activation but the following broad observation may be worth considering. Calculations suggest (see Figure 2) a fairly well defined ground state in a steep-sided energy well. The transition state is broad and rather flat and may have many ways through it, differing little in energy. These two factors should lead to a positive entropy of activation which would further improve the agreement between calculated and measured barriers.

Experimental

N.m.r. spectra were recorded on a Varian Associates XL200 spectrometer operating at 200 MHz for protons. Low-temperature spectra were recorded for solutions *ca.* 0.05M in *ca.* 1:1 $CHFCl_2$–CHF_2Cl. Temperature measurement at very low temperatures was done by inserting a thermocouple into the n.m.r. tube to the depth corresponding to the radiofrequency coil, then allowing the tube to reach a temperature equilibrium in the spectrometer probe without spinning. We estimate an uncertainty of *ca.* 3 °C in temperature quoted, although successive low temperatures no doubt differ by an amount quite close to the difference implied by the numbers quoted.

The calculations of conformational energies and structures were made using Allinger's MM2 programme.[11]

2-*t-Butyl*-2-(1-*naphthyl*)-1,3-*dioxolane* (**15**), and the known compound (**10**),[19] were prepared from naphthyl t-butyl ketone[20] by standard reactions, namely direct condensation with the glycol with azeotropic removal of water, and Clemmensen reduction, respectively. Compound (**15**) is a crystalline solid, m.p. 184 °C (Found: C, 79.4; H, 7.9. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.9%).

Relaxation times T_1 were measured by the inversion recovery method for 2- and 8-H, and those in the side-chain for compound (**10**). Proton–proton nuclear Overhauser enhancement was observed with pre-irradiation of the signal concerned for 30 s followed by a 90° pulse and acquisition without double irradiation. A control experiment was created with irradiation away from any signal, and a difference spectrum was obtained by subtraction of the control from each double irradiation experiment. Repetition of this many times, usually more than 400, allowed the calculation of the percentage nuclear Overhauser enhancement with considerable accuracy even when the value is $<1\%$. A line broadening of 2 Hz was used.

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