

The Back-and-forwards Flipping of *t*-Butyl Groups in 1,8-Di-*t*-butylnaphthalenes

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A dynamic n.m.r. investigation of a derivative of 1,8-di-*t*-butylnaphthalene shows that it has a barrier to back-and-forward flipping of *t*-butyl groups of 22.5 kcal mol⁻¹, in good agreement with molecular mechanics calculations.

1,8-Di-*t*-butylnaphthalene and its derivatives are so strained that the *t*-butyl groups are grossly displaced on opposite sides of the mean plane of the naphthalene ring¹ as in (1), and there is a barrier, originally thought to be at least 24 kcal mol⁻¹,² to the process that flips the *t*-butyl groups through the plane of the ring, (1)⇌(2). Our earlier work acknowledged³ some uncertainty in this uncommonly high barrier since it was derived from dynamic n.m.r. measurements on compound (3), which were unfortunately confused by the temperature dependence of chemical shifts. In contrast the barrier to rotation of the *t*-butyl groups in the *peri*-position, at 6.3 kcal mol⁻¹, is low for groups of this size, apparently close together.

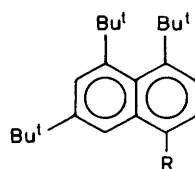
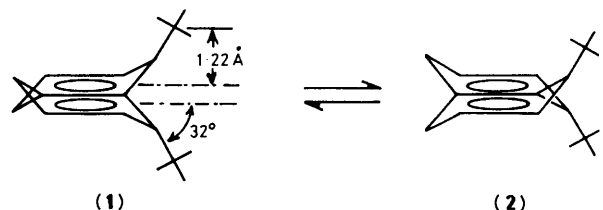
Interest in such molecules has continued recently with molecular mechanics studies,^{1,4} and with investigations of analogues (6)–(8). These three compounds have been synthesized^{5–7} and investigated by dynamic n.m.r. studies,^{8,9} by *X*-ray crystallographic structure determinations,¹⁰ and by molecular mechanics calculations.^{4,10} In these compounds, barriers to rotation of the M(CH₃)₃ groups are smaller than in (4),^{8,9} although molecular mechanics calculations predict a series of barriers changing in the opposite sense to that observed.¹⁰ In none of (6)–(8) was a process similar to the (1)⇌(2) flip observed. We now want to report further and more definitively on this unusual conformational process which racemizes the enantiomeric structures (1) and (2).

If the barrier to flipping be greater than *ca.* 24 kcal mol⁻¹, it was reasonable to hope to resolve and examine enantiomers of (1), and we put much effort into attempts at this with functionalised derivatives of (1).† Both chromatography over chiral stationary phases, and the separation of diastereoisomeric derivatives, were unsuccessful. We therefore decided to reinvestigate the flipping (racemisation) process by n.m.r. and in the event prepared a derivative of (5) with a different probe of chirality, *viz.* (4).‡ Our observations thereon give a clear picture of the conformational process.

The striking feature of the spectrum§ of (4) is a doublet (δv 10.6 Hz at ambient temperature) for the two methyls of the C(CH₃)₂OH substituent. This relative shift is temperature dependent (δv 7.5 Hz at 100 °C), but above 100 °C the peaks of the doublet broaden and coalesce at *ca.* 144 °C to a singlet,

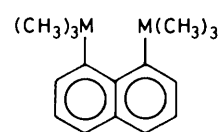
† We are grateful to Drs. H. W. Pirkle, E. Gil Aviv, and A. Mannschreck, for direct help, or advice in this aspect of our work.

‡ Compound (4) was prepared from 1,6,8-tri-*t*-butylnaphthalene² by bromination (Br₂–FeBr₃) to give the bromo-derivative of (4) which was converted into the cyano-derivative by treatment with copper(i) cyanide in dimethylformamide. The cyano-derivative on hydrolysis with base gave the carboxylic acid, the ester of which gave (4) on treatment with excess of methyl-lithium. Compound (4) is a high boiling liquid which is apparently dehydrated on heating and cannot be distilled even at reduced pressure. A sample, satisfactorily pure for n.m.r. purposes, showed a parent peak in its mass spectrum at *m/z* 254.2925 (C₂₅H₃₈O requires *M*, 354.292 25).



(3) R = CH₂Ph

(4) R = C(CH₃)₂OH



(5) M = C

(6) M = Si

(7) M = Sn

(8) M = Ge

indicating that the barrier to flipping is 22.5 kcal mol⁻¹ at that temperature. These spectral changes are reversible.¶

While, in the compound (4), there may be a small contribution to the barrier to flipping (1)⇌(2), from the substituent which forms the probe of chirality, we can now conclude that the barrier to flipping in 1,8-di-*t*-butylnaphthalenes is 22 kcal mol⁻¹, which is in good agreement with that of 18.5 kcal mol⁻¹ calculated by molecular mechanics methods¹ particularly when allowance is made for a probably negative entropy of activation.∥ This barrier suggests that the separation of enantiomers of (1) or its derivatives, would require experiments at rather lower temperatures than we used in our exploratory work.

§ At 200 MHz in deuterated nitrobenzene solution. In detail, singlets each equivalent to 9 H at δ 1.14, 1.19, and 1.40; singlets equivalent to 3 H at 1.88 and 1.93; a set of doublets equivalent to 4 H at 7.0–8.5. The OH signal is probably merged with that of traces of water, an impurity in the solvent.

¶ At temperatures above 100 °C, a non-reversible reaction becomes apparent, and it goes to completion after a few minutes at 160 °C. Analysis of the n.m.r. spectrum of the product suggests that elimination of water is taking place to give 4-isopropenyl-1,6,8-tri-*t*-butylnaphthalene, δ 1.19, 1.22, and 1.34 (3 × Bu^t), 2.10 (allylic Me), 4.96br and 5.28br (2 × CH), and 7.0–8.3 (ArH).

∥ An entropy of activation of –8.4 cal mol⁻¹ K⁻¹ is required to convert an enthalpy of activation of 18.5 kcal mol⁻¹ into a free energy of activation of 22 kcal mol⁻¹ at 144 °C.

Acknowledgements

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References

- 1 J. Handal, J. C. White, R. W. Franck, Y. H. Yuh, and N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 3345.
- 2 J. E. Anderson, R. W. Franck, and W. L. Mandella, *J. Am. Chem. Soc.*, 1972, **94**, 4608.
- 3 See footnote 16 in ref. 2.
- 4 M. G. Hutchings and I. Watt, *J. Organomet. Chem.*, 1979, **177**, 329.
- 5 (a) D. Seyferth and S. C. Vick, *J. Organomet. Chem.*, 1977, **141**, 173;
(b) R. J. Wroczynski, M. W. Baum, D. Kost, K. Mislow, S. C. Vick, and D. Seyferth, *ibid.*, 1979, **170**, C29.
- 6 F. Cozzi, U. Sjøstrand, and K. Mislow, *J. Organomet. Chem.*, 1979, **174**, C1.
- 7 R. Sooriyakumaran and P. Boudjouk, *Organometallics*, 1982, **1**, 218.
- 8 F. A. L. Anet, D. Donovan, U. Sjøstrand, F. Cozzi, and K. Mislow, *J. Am. Chem. Soc.*, 1980, **102**, 1748.
- 9 F. A. L. Anet, R. Sooriyakumaran, and P. Boudjouk, personal communication.
- 10 J. F. Blount, F. Cozzi, J. R. Damewood, L. D. Iroff, U. Sjøstrand, and K. Mislow, *J. Am. Chem. Soc.*, 1980, **102**, 99.

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