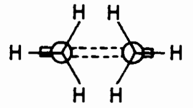
peri-Interaction, *ortho*-Interaction, and Barriers to Internal Rotation. A Dynamic Nuclear Magnetic Resonance and Molecular Mechanics Investigation of 1,2-Dineopentylbenzene and 1,8-Dineopentylnaphthalene

J. Edgar Anderson and David J. D. Barkel
Chemistry Department, University College, Gower Street, London WC1E 6BT
Flemming S. Jørgensen
Department of Chemistry BC, Royal Danish School of Pharmacy, Universitetsparken 2, DK-2100 Copenhagen, Denmark

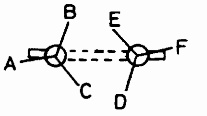
For 1,2-dineopentylbenzene and 1,8-dineopentylnaphthalene, barriers to interconversion of enantiomeric *trans*-conformations of 5.8 and 7.4 kcal mol^{-1} respectively have been measured by the dynamic n.m.r. method. Molecular mechanics calculations of the two molecules are reported and the results are discussed in terms of the relative importance of *peri*- and *ortho*-interactions.

The distance between *peri*-hydrogens in naphthalene[1] and that between *ortho*-hydrogens in benzene[2,†] is very similar as emphasised in Figure 1(a). When the hydrogens are replaced by substituents, longer diverging bonds from the benzene ring should increase the *ortho*-interaction distance relative to the *peri*-interaction distance, since this latter interaction reflects parallel bonds. In fact, in the dimethyl derivatives, the methyl–methyl distance is much the same, see the right-hand side of the Figure, but in the naphthalene molecule[3] this is at the expense of much greater bond-angle strain than is found in *ortho*-xylene.[4,‡]

The higher barrier to methyl group rotation in 1,8-dimethylnaphthalene[5] compared with *o*-xylene[4] (2.8 and 1.5 kcal mol^{-1}, respectively) is probably a consequence of the extra strain in the naphthalene case, implicitly even greater in the transition state than in the ground state. Both these dimethyl compounds have an unusual feature in that the hydrogens clash as in (**1**), even though they are within the van der Waals distance. For more highly substituted derivatives, interactions between substituents or with the ring are likely to ensure that a meshing conformation such as (**2**) (reflecting, no doubt, the nature of the substituents A—F) will be the more stable ground state. Thus the relative size of the barriers for methyl group rotation in the dimethyl compounds is not necessarily an indication of the strain in other substituted cases.

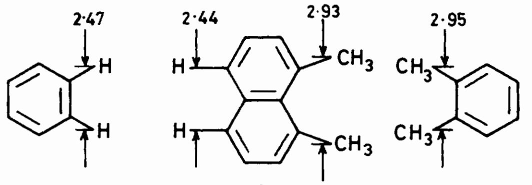


(**1**)



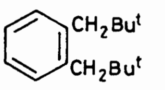
(**2**)

For benzenes[6] or naphthalenes[7] with more complicated substituents, a fruitful source of information on strain has been the study of rotational barriers, determined by the dynamic n.m.r. method. It is surprising however that there is no example where the same pair of substituents has been studied in the two series. We now report on the dineopentyl derivatives in both series, *ortho*-dineopentylbenzene (**3**) and 1,8-dineopentylnaphthalene (**4**).

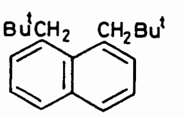


(*a*) (*b*) (*c*)

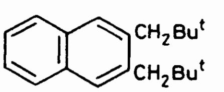
Figure. Distances in Å



(**3**)

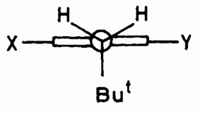


(**4**)

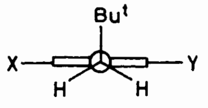


(**13**)

The neopentyl group is a particularly useful one for the study of the rotation of a planar group attached at an sp^2-hybridised carbon to an sp^3 centre.[8a] This arises because it can find two equivalent stable conformations close to structures (**5**) and (**6**) probably tilted somewhat away from the orthogonal representations shown, depending on the nature of X and Y. The transition state for rotation will be one in which the t-butyl group lies near to the plane of the ring. Whether it be to the X-side or the Y-side [as shown in structure (**7**)] depends on which side is the less hindered. Earlier work on 1,3,5-trineopentylbenzenes[8] and 1-neopentylnaphthalene[9,§] suggests that the transition state occurs not when the C–Bu^t bond is in the plane of the ring, but rather when the inward-pointing methyl of the t-butyl group passes through that plane as shown in structures (**7**) or (**8**).



(**5**)



(**6**)

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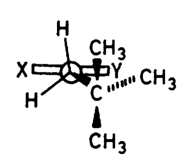
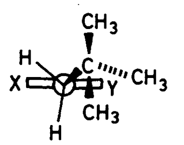
† $[1.397 + 2 \times 1.085 \sin 30°]$ Å^2.

‡ Ref. 4 reports a microwave determination of the structure and methyl rotational barrier, and refers to earlier measurements.

§ In ref. 9 we suggest a transmission coefficient for rotation t = 0.5 and thus a barrier of 5.15 kcal mol^{-1}. We now believe that a transmission coefficient t = 1 and a barrier of 5.3 kcal mol^{-1} is correct. There are two equivalent transition states at *ca.* 40° on either side of the t-butyl in-the-plane conformation. Passage through either of these (t = 1) not both of these (t = 0.5) brings about interconversion of conformation.



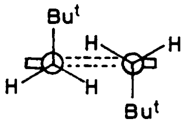
(7)



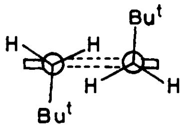
(8)

When only one neopentyl group is involved, the barriers have already been investigated by the dynamic n.m.r. method. The barrier to rotation in 1-neopentylnaphthalene is 5.3 kcal mol^{-1},[9] while that in neopentylbenzene[10] is less (probably much less) than 6.0 kcal mol^{-1}.

When there are two neopentyl groups as in (**3**) and (**4**), the question arises as to whether there are two possible kinds of stable conformation, *cis*, with the t-butyl groups on the same side of the plane and *trans*. The *cis*-form seems unlikely when the neopentyl groups are as close as in (**3**) or (**4**), but we will examine their n.m.r. spectra for indications of such conformations. In the absence of a *cis* conformation, the dynamic process examined by n.m.r. spectroscopy is a double rotation interconverting two enantiomeric *trans* conformations approximating to structures (**9**) and (**10**).

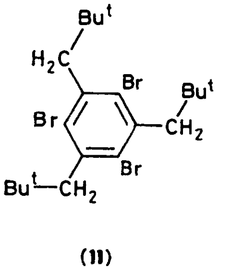


(9)

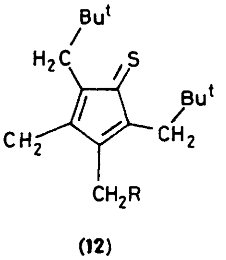


(10)

The possible existence of a stable *cis* conformation has added interest in that a *cis* arrangement with the correct separation of neopentyl groups is well set up for attractive steric interactions, as has been shown in two cases; see (**11**)[11] and (**12**).[12] The neopentyl groups are rather further apart than in (**3**) or (**4**).



(11)



(12)

A previous study of a 1,2-dineopentylbenzene rotation exists,[13] there being a barrier of 16.2 kcal mol^{-1} to the interconversion of enantiomeric *trans* conformations for 3,4,5,6-tetramethyl-1,2-dineopentylbenzene.

Molecular mechanics calculations have provided much useful information on the ground-state structures, strain, and rotational barriers for alkylbenzenes and alkylnaphthalenes.[8,9,13,14] Calculations of structural parameters give a reliable indication of reality,[14] so we have used Allinger's MM2/82 program[15] to predict conformations for (**3**) and (**4**).

Results

Dynamic N.M.R. Spectroscopy.—The proton n.m.r. spectrum of (**4**) comprises a complex aromatic region from δ 7.3—7.5 and two singlets of relative intensity 4.5:1 at δ 0.81 and 3.39 assigned to the t-butyl and methylene hydrogens, respectively. Below *ca.* −60 °C, the latter signal broadens and splits at about −103 °C to a spectrum which appears as a broad AB system at −130 °C $\delta_A = 4.10$, $\delta_B = 2.68$, $J_{AB} \sim 13.5$ Hz.

Table. Molecular mechanics calculations of the minimum-energy *trans*-conformation of 1,8-dineopentylnaphthalene (**4**) and 2,3-dineopentylnaphthalene (**13**)

	trans-Conformation of	
Energy terms/kcal mol^{-1}	1,8-Dineopentylnaphthalene	2,3-Dineopentylnaphthalene
Total steric energy	9.89	−1.00
Bond compression	2.56	1.90
Bond bending	6.56	2.95
Bond stretch/bend	0.43	0.33
van der Waals 1—4	13.49	12.95
van der Waals other	−3.61	−4.63
Torsional	−9.59	−14.50
Dipolar	0.03	0.10
Geometric terms/°		
Angle CH$_2$–Bu^t and mean plane	79.5	98.4
Angle CH$_2$–C$_{Ar}$–C$_{Ar}$	126.0	123.6
Angle C$_{Ar}$–CH$_2$Bu^t	115.2	115.6
Mean variation from 60° of CH$_2$Bu^t dihedral angles	3.1	0.5

There was no indication of a second AB-system for the CH$_2$ group nor of a second singlet for the t-butyl group, nor of unusual broadening of the t-butyl signal at any low temperature. The absence of such signs allows us to exclude the presence of a second, *cis*, conformation.

From the changes in the methylene signal the rate constant for the interconversion of conformation (**9**) and its mirror image (**10**) is 637 s^{-1} at −103 °C. Assuming a transmission coefficient of 0.5 (see below) the barrier to the conformational process is 7.35 kcal mol^{-1}.

The proton n.m.r. spectrum of 1,2-dineopentylbenzene (**3**) comprises two singlets of relative intensity 4.5:1 at δ 0.91 and 2.62 for the t-butyl and methylene protons, respectively and an AA′BB′ aromatic spectrum at δ 7.1—7.5. As the temperature was lowered below *ca.* −130 °C, the methylene signal broadened relative to SiMe$_4$ and it appeared as a broad doublet (δ ~ 70 Hz at 200 MHz) at −149 °C. At lower temperatures, spectral quality was poorer.

The methylene signal should appear as an AB-system when rotation is slow. Assuming that the observed 70 Hz separation represents the inner lines of the AB-system, and a coupling constant *J* of 13.5 Hz as found for (**4**), a relative chemical shift δ_v of 82 Hz can be calculated. From these figures the rate constant for interconversion at the coalescence temperature, −143 °C, is 197 s^{-1}. From this value (assuming a transmission coefficient of 0.5) the free energy of activation for bond rotation is 5.8 kcal mol^{-1}.

Molecular Mechanics Calculations.—We have used the Allinger MMP2/82 force field and program[16] to give a quantitative indication of the steric interactions in certain interesting conformations of (**3**) and (**4**). To eliminate irrelevant differences we have compared calculations for (**4**) and 2,3-dineopentylnaphthalene (**13**) and some details of their minimum-energy *trans*-conformations are shown in the Table.

The relative magnitudes of the steric energy of the *trans*-1,8- and the *trans*-2,3-conformations (9.89 and −1.00 kcal mol^{-1}, respectively) is a clear indication of how much a *peri*-interaction is greater than an *ortho*-one. The difference of 10.89 kcal mol^{-1} is, as expected, much greater than that found earlier[9] for 1- and 2-neopentylnaphthalene (3.1 kcal mol^{-1}).

All components of the steric energy (except the negligible dipole contributions) are less favourable in the *peri* series.

The main difference in steric strain calculated for (**4**) and (**13**) comes from the bond angle distortion and torsional strain terms, indicating that these are the least energy-expensive way of distorting to reduce steric interactions. Geometric parameters fit with this energy picture, although the differences are quite small.

We applied the dihedral drive option of the Allinger program to one of the sp^2–sp^3 bonds in (**13**) to rotate one neopentyl group away from the second so that its t-butyl group passed progressively from the stable *trans* conformation through the plane to an energy minimum with the t-butyl groups *cis*.

Most interestingly, *cis*-conformations for (**13**) turn out to be only slightly more stable (H_{trans} + 4.25 kcal mol^{-1})* than the rotational transition state which has an inward-directed methyl group in the plane of the ring as in (**7**) or (**8**) (H_{trans} + 5.20 kcal mol^{-1}).† The encounter with the second neopentyl group in the *cis*-conformation results in both t-butyl groups tilting away from each other nearer to the plane, and is about as disfavourable as the encounter with the naphthalene plane during rotation. Thus the two enantiomeric *trans*-conformations are well defined minima separated by the broad plateau of the coplanar and *cis* conformations, with many small local maxima and minima reflecting the interactions of the t-butyl groups.

Determining the overall minimum-energy *cis*-conformation and the most favourable pathway between the two stable *trans*-conformations would require a thorough exploration of this region which we decided not to undertake.

When the dihedral drive option was applied to (**4**), the first minimum-energy *cis*-conformation encountered is less stable than the *trans*-conformation by a comparable amount (4.80 kcal mol^{-1}).

Discussion

It is striking how similar the experimental rotational barriers are (7.4 and 5.8 kcal mol^{-1}), when the ground-state strain appears to be so different (by 10.89 kcal mol^{-1} by calculation). This similarity in barriers may arise since the main cause of the barrier is a t-butyl group passing through the plane of the aromatic ring remote from the second neopentyl substituent. In both cases this should give rise to similar interactions. It is the CH_2-part of the rotating neopentyl group which experiences differing interactions in the two cases, mainly with the second neopentyl group. It is not immediately obvious that the change in these interactions should be greater in the *peri*-substituted case, but it is relevant that the difference in barriers found here (1.6 kcal mol^{-1}) is similar to that found in the *o*-xylene–1,8-dimethylnaphthalene comparison (1.3 kcal mol^{-1}) mentioned in the Introduction. We should perhaps avoid making too much of this similarity since the rotations described are putatively twofold and threefold, respectively.

It does seem to be however that for the dineopentyl compounds one part of the substituent contributes the larger part of the barrier, while the other part determines the difference in barrier, and all this has to be set beside a calculated difference in ground states much larger than either barrier. It certainly urges against predicting or interpreting the relative magnitude of rotational barriers on the basis of the perceived degree of crowding in the ground state.

The *cis*-conformation in each case is calculated to be noticeably less stable than the *trans* [by 4.25 and 6.22 kcal mol^{-1} for (**13**) and (**4**) respectively. We did not explore the *cis* hypersurface for better minima.] This is as expected, for t-butyl groups appear to be too close together, and the cases where attractive interactions between t-butyl groups were observed[11,12] involved groups attached to an *anti,anti*-1,5-planar arrangement of bonds rather than the *cis,cis*-1,5-arrangement of (**4**) or the *cis*-1,4-arrangement of (**13**).

Experimental

Spectra were recorded for *ca.* 0.01M solutions of the neopentyl compound in a mixture of approximately 4:4:1 chlorodifluoromethane–dichlorofluoromethane–[$^2H_6$]dichloromethane, on a Varian XL200 n.m.r. spectrometer operating at a frequency of 200 MHz. 1,2-Dineopentylbenzene (**3**) was a generous gift from Dr. F. van Rantwijk, University of Delft.[17] 1,8-Dineopentylnaphthalene (**4**) was prepared from 1,8-bis(bromomethyl)naphthalene[18] and t-butyl-lithium by the method of Martinson,[19] as a yellow oil which appeared to be a single compound by n.m.r. spectroscopy (Found: M^+, 268.2177. Calc. for $C_{20}H_{28}$: *M*, 268.2191).

The comparison of free energies of activation measured at temperatures differing by 40 °C is justified only if the entropy of activation is small. Rotation of t-butyl groups usually involves negative entropies of activation (in the case of Bu^tCMe_2Cl for example, −7.2 cal mol^{-1} K^{-1} [20]). Such a value for (**3**) and (**4**) (which reasonably should have values of comparable magnitude) would change the comparison to free energies of activation of 7.35 and 6.1 kcal mol^{-1} at −103 °C.

Rate constants, at the coalescence temperature in each case, were calculated from the equation $k = \lambda[(\delta^2 + 6J^2)^{\frac{1}{2}}]/\sqrt{2}$. Barriers are free energies of activation at the coalescence temperature.

Acknowledgements

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* $\Delta H_f^\circ(cis) = \Delta H_f^\circ(trans)$ + 4.25 kcal mol^{-1}.

† $\Delta H_f^\circ(\text{t.s.}) - \Delta H_f^\circ(trans)$ = 5.20 kcal mol^{-1}.

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