peri-Interactions in Naphthalene Derivatives. Rotation in 1,8-Disubstituted Naphthalenes

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Summary Structural features giving rise to low and high barriers in the compounds mentioned in the title are illustrated.

In a naphthalene with substituents in both the 1- and 8-positions, steric interactions are inevitably great, but barriers to rotation of the substituents are not always high.

In compound (**1**) the barrier is[1] 17·3 kcal mol^{-1} whereas in compounds of the type (**2**)[2] it is only about 6·3 kcal mol^{-1}. Planar substituents as in (**1**) can arrange themselves parallel to each other and nearly orthogonal to the mean plane of the naphthalene ring to give a relatively low-energy ground state; in (**2**) there is no obvious low-energy conformation. For both (**1**) and (**2**) the interactions in the transition state for rotation are no doubt high and it has been suggested[2] that the very different barriers reflect differences in strain in the ground state.

We and others† have studied further naphthalenes (**3**)—(**6**) and found that the barrier to rotation appears to be too low to be measured by the n.m.r. method (*i.e.*, <6—8 kcal mol^{-1}). The spectra did not show any significant changes at low temperatures; if signals are accidentally isochronous, the barrier may be higher than the upper limit given. Of these compounds, (**3**) and (**4**) have planar substituents while (**5**) and (**6**) have tetrahedral ones.

One may reasonably conclude that in (**3**) and (**4**) in the

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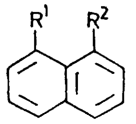
† The results for (**3**), (**4**), and (**5**) are reported for the first time. The results for (**6**) have been reported elsewhere (J. B. Robert, J. S. Sherfinski, R. E. Marsh, and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 1152) and agree with our observations for the same compounds.

likely transition state for rotation, *i.e.*, with one planar substituent in the mean plane of the naphthalene ring, the interactions are less than in (**1**) since the planar cross section of the substituent is smaller.



(**1**) R^1 = Ph, R^2 = C_6H_4·CMe$_2$OH-*m*
(**2**) R^1 = R^2 = CMe$_3$
(**3**) R^1 = R^2 = CO$_2$Et
(**4**) R^1 = R^2 = C(O)Et
(**5**) R^1 = R^2 = CHMe$_2$
(**6**) R^1 = R^2 = CH$_2$X
(X = H, OH, Br, or I)
(**7**) R^1 = CHMe$_2$, R^2 = CO$_2$Me
(**8**) R^1 = CH$_2$Ph, R^2 = C(O)Ph
(**9**) R^1 = CH$_2$OH, R^2 = C(:CH$_2$)Me

In the cases of (**5**) and (**6**) with tetrahedral substituents, a second feature becomes important. There are now two possible barriers to rotation, and n.m.r. spectroscopy detects the lower of these. If this is $\lesssim$6—8 kcal mol^{-1}, then no matter how high the higher barrier, the n.m.r. spectrum will show no changes. In both (**5**) and (**6**) the low-energy barrier involves hydrogen atoms rotating through the gap between the 1- and the 8-substituent, while the high-energy process involves a methyl group in (**5**) or the group X in (**6**) moving through this gap. This explanation resembles that already adduced for 1,8-bisdimethylaminonaphthalene.[3]

The negative results for (**3**)—(**6**) and the explanations for these that we offer suggest that measurable high barriers to rotation should be found in compounds similar to (**3**)—(**6**) but with one planar and one tetrahedral substituent.

The isopropyl methyl groups of (**7**) appear as a doublet (J 6·5 Hz) at δ 1·28 at ambient temperature. Below −100 °C this signal appears as two equal doublets of relative chemical shift 17 Hz,‡ indicating that the barrier to rotation of the ester group is 8·9 kcal mol^{-1}.

At ambient temperature the CH$_2$ signal for (**8**) is a singlet at δ 4·03 which splits below −30 °C into an AB quartet (δ_{AB} 16·5, J_{AB} 16·0 Hz) indicating that the barrier to rotation of the benzoyl group is 11·9 kcal mol^{-1}.‡

The CH$_2$ protons of the CH$_2$OH group in (**9**) appear as an AB quartet (δ_{AB} 38, J_{AB} 13·9 Hz) at δ 5·17 at room temperature.‡ These signals coalesce to a singlet at 76 °C indicating a barrier to rotation of the isopropenyl group of 17·3 kcal mol^{-1}.

In these three examples, the barrier reported is the lower of the two barriers to rotation of the planar group, irrespective of the rate of rotation of the tetrahedral group. The results indicate that it should be possible to decide in which of the title compounds barriers to rotation are likely to be high.

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‡ Spectra were recorded at 100 MHz; barriers were calculated from coalescence temperatures for AB quartets, otherwise by full lineshape treatment. Satisfactory analyses have been obtained for all new compounds.

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