Hindered Rotation in 1-Alkenyl-naphthalene Analogues of Binaphthyl; A Dynamic N.M.R. Study

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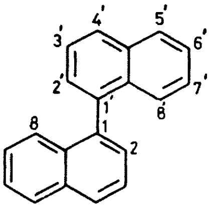
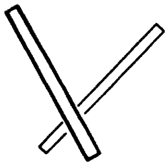
Summary Barriers to rotation in some 1-alkenyl-naphthalenes are greatly dependent on both direct and buttressing effects of the substituents on the olefin

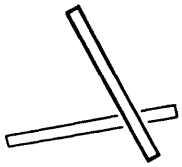
High barriers to rotation in binaphthyls (**1**) are one of the classic examples of steric hindrance in organic molecules.[1–3] In the parent compound, the barrier to rotation [*i.e.* (**2**) $\rightleftharpoons$ (**3**), viewed along the 1–1′ bond][4] is 23·5 kcal/mol,† the forms (**2**) and (**3**) being chiral. This property has been used as a control of stereochemistry in a range of investigations.[5]



(**1**)



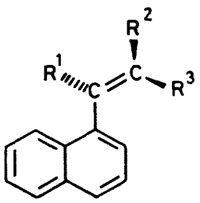
(**2**)



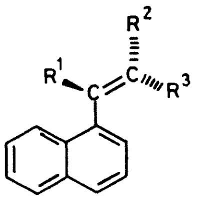
(**3**)

During rotation through a more-or-less planar transition state (**1**), the remote part of the second naphthalene ring (that is carbons 3′ to 7′) should contribute little to the interactions encountered by the first naphthalene ring. This led us to expect that there might be high barriers to rotation in any 1-substituted naphthalene where the substituent resembles the bottom part of the upper naphthalene ring shown in (**1**), that is where there is a planar substituent of some bulk. Alkenyl naphthalenes form such a system, and we now report preliminary results showing a wide range of barriers to rotation in the systems (**4**) $\rightleftharpoons$ (**5**), which depend on the size of R^1 and R^3, and an unusually large buttressing effect of the remote substituent R^2. There is some scant information in the literature on aza-analogues[6] and cyclic analogues[7] of (**4**). We used the dynamic n.m.r. method to determine barriers to rotation. Temperature-dependent spectra which allow the determination of these barriers can be expected only when one of the substituents R^1, R^2, or R^3 contains groups which are diastereotopic when rotation (**4**) $\rightleftharpoons$ (**5**) is slow on the n.m.r. time-scale, so suitable substituents were chosen.

Results obtained are shown in the Table. As a typical example of the spectral changes observed, the isopropyl methyl signal for (**6c**) at room temperature comprises two doublets (*J ca.* 7 Hz) at δ 0·79 and 1·135. These doublets broaden as the temperature is raised, coalesce at about 48 °C and appear as a single sharp doublet (*J ca.* 7 Hz) at δ 0·96 at 70 °C. There were no other significant changes in the spectrum. A complete lineshape analysis of these changes gave a barrier to rotation of 16·1 kcal/mol.

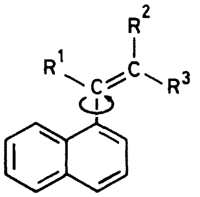


(**4**)



(**5**)

Table. Barriers to rotation[a] (in kcal/mol) in the alkenylnaphthalenes (**6**) and (**7**).



	(**6**) $R^1 = Pr^i$	(**7**) R^1 = Et
a; $R^2 = R^3$ = Me	>>26·0	25·8
b; R^2 = H, R^3 = Me	21·1	12·2
c; R^2 = Me, R^3 = H	16·1	<7·0
d; $R^2 = R^3$ = H	11·5	<7·0

[a] Barriers are free energies of activation at the following temperatures (°C) for (**6a**—**d**) and (**7a**—**d**), respectively: 200, 165, 48, −61; 195, −48, −151, −156.

It is clear from the results in the Table that the height of the barrier depends greatly on the size of R^1 and R^3, presumably by virtue of their direct interaction with hydrogens in the 2- and 8- positions of the naphthalene ring, in a way which recalls the substituted binaphthyls.[2] What is less expected is the effect of the substituent R^2, where replacement of a hydrogen atom by a methyl group leads to a barrier which is higher by between 4·6 kcal/mol [(**6b**) *vs.* (**6a**), (**6d**) *vs.* (**6c**)] and more than 13 kcal/mol [(**7b**) *vs.* (**7a**)]. The buttressing effect of R^2 is presumably a result of constraint being placed on the conformations adopted by R^1 and R^3 during rotation, which affects the interactions of these groups with the naphthalene ring.

The addition of only two methyl groups leads from a molecule (**7c**) where rotation is fast on the n.m.r. time-scale even at −140 °C, to a molecule (**6a**) which should be capable of resolution into optical isomers that are stable at room temperature.

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† 1 cal = 4·184 J.

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[2] W. Dixon, M. M. Harris, and R. Z. Mazengo, *J. Chem. Soc.* (*B*), 1971, 775.

[3] A general review of peri-interactions is given by V. Balasubramaniyam, *Chem. Rev.*, 1966, **66**, 567.

[4] A. S. Cooke and M. M. Harris, *J. Chem. Soc.* (*C*), 1967, 988.

[5] Widely differing examples are (a) on chiral reducing reagents; R. Noyori, I. Tomino, and Y. Tanimote, *J. Am. Chem. Soc.*, 1979, **101**, 3129, and (b) on host-guest complexation; Y. Chao, G. R. Weisman, G. D. Y. Sogah, and D. J. Cram, *ibid.*, p. 4948 and references cited therein.

[6] D. R. Boyd, S. Al-Showiman, and W. B. Jennings, *J. Org. Chem.*, 1978, **43**, 3335 and references cited therein.

[7] D. Nasipuri, P. K. Bhattacharya, and G. T. Furst, *J. Chem. Soc., Perkin Trans.* 2, 1977, 356.