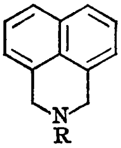
peri-Interaction in Naphthalene Derivatives: Dihydrobenzisoquinolines

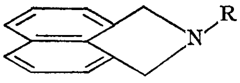
By J. E. ANDERSON*
(*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California,* 91109)
and A. C. OEHLSCHLAGER
(*Department of Chemistry, Simon Fraser University, Burnaby* 2, *B.C., Canada*)

THERE is strain inherent in naphthalenic compounds due to the interaction of substituents in the 1 and 8 positions.[1] We have studied some compounds in which, because of this strain, conformational processes may be slow, *e.g.* 2-alkyl-2,3-dihydro-1*H*-benz[*de*]isoquinolines (I), a series of compounds derived from naphthalimides by lithium aluminium hydride reduction.[2] Our study uses n.m.r. spectra at several temperatures, a technique suitable for the study of equilibria with activation energies of between about 5 and 25 kcal./mole.[3]

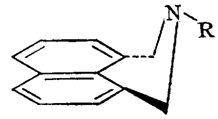
Little is known of the conformation of compounds of type (I), the general possibilities being represented by (II) and (III). Distortions both out of the plane (II), and in the plane of the aromatic system (III) are known in naphthalene derivatives,[1] so that some conformation intermediate between (II) and (III) is probably correct. For the most stable conformation [torsional strain is greater in (II), so our results are discussed in terms of (III)], there is a mirror-image conformation of the same energy, for example (III) and (IV), and interconversion of these is possible by a ring inversion and a nitrogen inversion, (III) $\rightleftharpoons$ (V) $\rightleftharpoons$ (IV) or (III) $\rightleftharpoons$ (VI) $\rightleftharpoons$ (IV). (V) and (VI) should be of higher energy than (III) and (IV) due to nonbonded interactions between R and the aromatic ring.



(I)



(II)

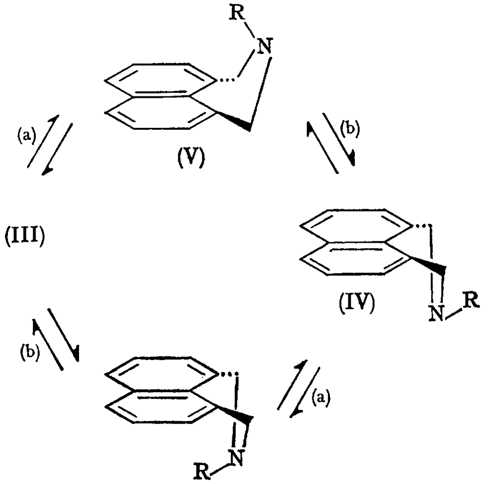


(III)

Associated with these two inversions are strains, one due to distortion of the ring, and the other to distortion of the conformation at the nitrogen and a different ring distortion. These inversions could occur consecutively during interconversion to give a two-part barrier rather than simultaneously to give a single high barrier. The energy maximum on the reaction profile will be at whichever of the two transition states has higher energy.

The changes were observed for several compounds (I) where R is an alkyl substituent; in this discussion R = methyl, (Ia).[2]

A chloroform solution of (Ia) at ambient temperature shows in its n.m.r. spectrum, singlet peaks at δ 2·57 (N–Me), and δ 3·90 (Ar–CH_2–N), and a complex of peaks around δ 7·40 from the aromatic hydrogens. Below about −40°, the Ar–CH_2–N signal broadens and splits about −72° to give a broad AB-quartet (δ_{AB} 0·55 p.p.m., J_{AB} 15·5 Hz).† The free energy of activation for the process is 9·7 kcal./mole at −72°.[3]



(a) Nitrogen inversion
(b) Ring inversion

The spectrum does not show whether nitrogen inversion or ring inversion is the rate-determining step in the conformational equilibrium. However, it is known[4] that barriers to nitrogen inversion vary markedly with solvent, while molecules which contain nitrogen atoms, but are known to be undergoing ring inversion, have barriers which are more or less independent of solvent.[5] The effect of solvents on the barrier to the interconversion process is shown in the Table, and suggests that nitrogen inversion is the rate-determining step.

TABLE

The effect of solvents on the barrier to inversion of (Ia).

Solvent	Coalescence temperature, T_c°	$\Delta G^*_{T_c}$ (kcal./mole)
$CDCl_3$	−72	9·7
CD_3OD	−62	10·2
13%D_2O/CD_3OD	−56	10·6
31%D_2O/CD_3OD	−50	10·9

Barriers to nitrogen inversion are usually too small to be measured by the present technique, so that in piperidine is unknown. The barrier becomes measureable, when the strain within the molecule does not favour the planar transition-state conformation at the nitrogen atom.[6] Here the nitrogen atom, to become planar, must force

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† Even at the slow exchange limit, line widths are 3—4Hz. Broadening is expected due to coupling with the N–Me group, and mutual coupling between the two methylene groups, as well as coupling of the order 1 Hz with *o*- and *p*-ring hydrogens, *cf.* H. Prinzbach, V. Freudenberger, and U. Scheidegger, *Helv. Chim. Acta*, 1967, **50**, 1087.

apart the *peri*-CH_2 groups, and consequently distort the aromatic system. The strain involved causes the measurable barrier to nitrogen inversion, and this novel demonstration of the *peri*-effect.

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