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CONFORMATIONAL STUDIES BY DYNAMIC NMR. PART 29[1]. INTERCHANGE OF SYMMETRY BETWEEN THE GROUND AND EXCITED ROTATIONAL STATES OF THE ISOMERIC N,N-DIISOPROPYLNAPHTHYLAMINES.

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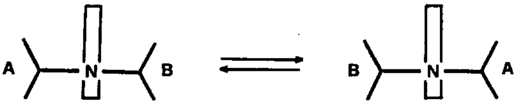
Summary: Low temperature NMR spectra show that the rotational ground state of N,N-diisopropyl -1-naphthylamine is perpendicular whereas that of its isomer (N,N-diisopropyl-2-naphthylamine) is planar: their rotational barriers have been measured (15.4 and 6.3 Kcal/mol respectively).

Non hindered aromatic amines adopt a conformation where the ring is coplanar with the dynamic plane containing the rapidly inverting nitrogen atom.[2] Rotation occurs through a perpendicular transition state: the corresponding free energies of activation have been recently measured in solution by NMR.[3-5] Aromatic amines hindered by ortho substituents are expected, on the contrary, to adopt a conformation with twisting angles close to 90°; rotation hence occurs through a planar transition state.[6,7]

We have here obtained direct evidence that N,N-diisopropyl-1-naphthylamine (**1**) belongs to the first class whilst its isomer, N,N-diisopropyl-2-naphthylamine (**2**), belongs to the second one, the interchange of the conformational symmetries being due to the different steric demand.

In fact the 300 MHz proton NMR spectrum of **1** displays, below 20°C, two doublets for CH_3 but only one multiplet (septet) for CH. Homodecoupling experiments confirm that below this temperature there is a single line for CH but a pair of lines for CH_3. The same behaviour is also observed by C-13 NMR (Figure). On raising the temperature the methyls become homotopic: the conformation of **1** has thus to be perpendicular (or librating with a negligible barrier about a perpendicular geometry) as indicated in the following scheme, where a top view of **1** is presented:



Whereas the two CH groups are always homotopic, the methyls within the isopropyl groups A and B become anisochronous when the interconversion is slow, owing to the absence of a molecular plane of symmetry bisecting the Me-CH-Me angle: the methyls are thus prochiral at low temperature. The process that renders the methyls homotopic is a C-N rotation that requires a passage through a coplanar transition state: the corresponding $\Delta G^{\neq}$, obtained by line shape simulation, is given in the Table.

The C-13 spectrum (at -145°) of the isomer **2** displays, on the other hand, two lines for both CH and CH_3. This implies the existence of a coplanar conformation where the two isopropyl groups experience different spatial environments. Equivalence of CH and CH_3 is reached above -135° by a rotational process through a perpendicular transition state. The much higher $\Delta G^{\neq}$ of **1** with respect to **2** depends on the steric effect due to H8, that enhances the energy of the planar transition state of **1** with respect to the perpendicular ground state.

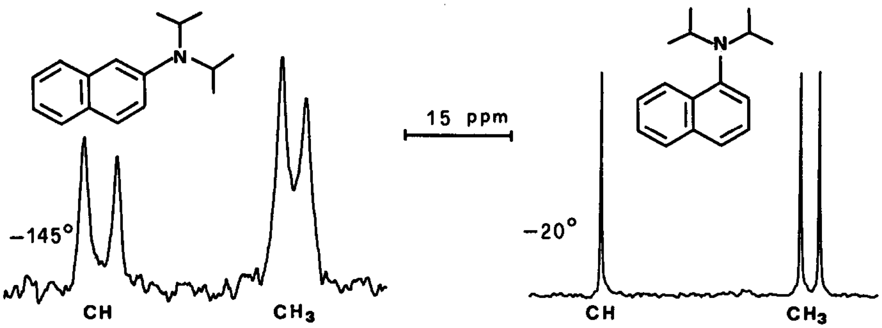


Figure. C-13 NMR spectra (25.2 MHz) of the aliphatic region of **2** in CHF_2Cl (left) and of **1** in $CDCl_3$ (right), taken at temperatures (-145° and -20° respectively) where the internal rotations are slow.

TABLE

	Solvent	Temperature range (°C)	$\Delta G^{\neq}$ (Kcal/mol)	Frequency (MHz)	$\Delta\nu$(CH) (Hz)	$\Delta\nu(CH_3)$ (Hz)
1	CS_2	+9, +24	15.4	300 (H-1)	-	17
1	$CDCl_3$	+6, +27	15.5	300 (H-1)	-	17.5
1	$(CD_3)_2CO$	+10, +30	15.5	300 (H-1)	-	18
1	$CDCl_3$	+19, +38	15.3	25.2 (C-13)	-	59
2	CHF_2Cl	-139,-135	6.3	25.2 (C-13)	114	86

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