

13C-NMR and theoretical studies of internal rotation in methylated anilines

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The conformational properties of ten ring-methylated N-methyl- and N,N-dimethylanilines have been studied using ^{13}C -NMR chemical shifts and spin-lattice relaxation times in CDCl_3 , and semi-empirical (AM1) quantum-chemical calculations. The experimental results indicate that, like aryl methyl ethers, N-methylanilines prefer conformations in which the N-methyl carbon lies near the ring plane. Ortho-substitution in these compounds, while forcing the N-methyl group to adopt an anti orientation with regard to the ortho substituent, does not induce any important changes from the vantage point of the electron donor ability of the amine function and therefore does not affect the N-methyl ^{13}C chemical shifts or spin-lattice relaxation times to any appreciable extent. The preferred conformations of ortho-unsubstituted N,N-dimethylanilines leave the N-methyl carbon atoms oscillating on either side of the ring plane, but the conformational space of these compounds is strongly limited by ortho-meth