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SOLVENT DEPENDENCE OF THE BARRIER TO THE Ph-N INTERNAL ROTATION IN N-METHYLANILINE

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Abstract: The barrier to Ph-N internal rotation in N-methylaniline in CF_2Cl_2 (from ^1H NMR) is 6.9 kcal/mol. Solvents which are hydrogen bond acceptors raise the barrier, while hydrogen bond donors lower the barrier.

The dynamic NMR behaviour of N-methylaniline (I) has been reported by our laboratory[2] and by that of Professor Lunazzi.[3] The two investigations employed different solvents (a $CHCl_2F$-CF_2Cl_2 mixture and dimethyl ether, respectively) and reported significantly different free energy barriers for Ph-N internal rotation (6.1 and 7.24 kcal/mol, respectively). In order to clarify these differences, we have determined the barrier to internal rotation in I in an inert solvent (CF_2Cl_2), as well as in dimethyl ether, $CHCl_2F$, and CHF_2Cl. A possible problem with secondary amines such as I is that the internal rotation can be catalyzed by a trace of amine salt, but this can be checked by noting whether the ^1H signal of the N-methyl is a doublet or a singlet. The addition of some basic alumina to the NMR tube is an excellent way[4] of assuring the absence of any amine salt.[5] With dimethyl ether as the solvent, essentially the same barrier as determined by Lunazzi *et al.* is obtained. With either $CHCl_2F$ or CHF_2Cl (plus CD_3COCD_3 for lock purposes) the barriers are significantly lower than with CF_2Cl_2 as the solvent (Table I).

Table I

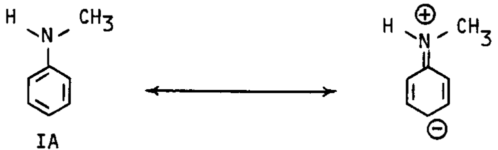
Barriers to the Ph-N Internal Rotation in N-Methylaniline Measured in Different Solvents

Solvent	Nucleus	Temperature °C	Barrier $\Delta G^{\ddagger}$ kcal/mol
CF_2Cl_2	^1H	-130 to -138	6.93 ± 0.05[a]
Me_2O (+ alumina)	^{13}C	-100 to -133	7.20 ± 0.04[b]
Me_2O	^{13}C	-113 to -126	7.24 ± 0.02[c]
CHF_2Cl (+ alumina)	^{13}C	-100 to -130	6.57 ± 0.04[b]
$CHFCl_2F$ (+ alumina)	^{13}C	-100 to -130	6.56 ± 0.04[b]
$CHFCl_2$-CHF_2Cl (1:4)	^{13}C	-135	6.1[d]

(a) From line shape analysis of 200 MHz ^1H NMR spectra (Bruker WP-200). (b) From line shape analysis of 50 MHz ^{13}C NMR spectra (Bruker WP-200). (c) Reference 3. (d) Reference 2.

Since dimethyl ether is expected to be a hydrogen bond acceptor and the Freons should be weak hydrogen bond donors (as is chloroform), we also used a Freon (CF_2Cl_2) without hydrogen. Because

CF_2Cl_2 is a poor solvent, we measured ^1H rather than ^{13}C NMR spectra. As shown in Table I, the barrier is lower than that in dimethyl ether, but higher than those in the hydrogen containing Freons.[6] These differences are qualitatively understandable since dimethyl ether should increase the double bond character of the Ph-N bond by the stabilization of the resonance structure IB (and related structure), because the positive charge on the NH group in IB should increase the acidity of that group. The Freons, $CHCl_2F$ or CHF_2Cl, should do the opposite because of stabilization of IA, via hydrogen bonding to the lone pair of electrons.


IA
IB

This explanation is supported by the larger upfield shift of the para ^{13}C chemical shift (i.e., larger negative charge[8]) in dimethyl ether as compared to the hydrogen-containing Freons. The proton chemical shifts of I in CF_2Cl_2 are given in Table II.

Table II

^{13}C and ^1H Chemical Shifts of N-Methylaniline in Different Solvents at Low Temperatures

Solvent	Nucleus	Temperature °C	Chemical Shifts, δ (ppm)						
			Me	C_1	ortho		meta		para
Me_2O	^{13}C	-100	30.3	150.9	112.4		129.9		116.6
		-133	30.3	150.9	109.3	115.3	129.6	130.4	116.6
CHF_2Cl	^{13}C	-100	30.9	150.9	113.4		130.4		117.8
		-150	30.9	150.8	110.9	116.6	130.0	130.7	117.2
$CHCl_2F$	^{13}C	-100	30.9	149.9	112.9		129.8		117.4
		-145	31.0	149.9	110.3	115.9	129.6	130.2	117.5
CF_2Cl_2	^1H	-110	2.74		6.47		7.03		6.49
		-145	2.74		6.39	6.55	6.97	7.09	6.49

References and Notes

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5. The N-methyl group of freshly distilled I was a singlet in ordinary $CDCl_3$ at room temperature, but become a sharp doublet on the addition of alumina.
6. The 6.1 kcal/mol barrier reported in reference 2 for $CHCl_2F$-CHF_2Cl is too low, possibly due to the presence of intermolecular exchange catalyzed by amine salts.
7. For recent theoretical calculations of the rotation barrier in aniline, see J. Gerhards, T.-K. Ha, and X. Perlia, Helv. Chim. Acta, 65, 105 (1982).
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