Tetrahedron Letters No.28, pp. 3227-3230, 1968. **Pergamon Press. Printed in Great Britain.**

INTERNAL ROTATION
ABOUT THE N-ARYL BOND IN ORTHO-DISUBSTITUTED ANILINES AND ANILINIUM IONS 1)

Albrecht Mannschreck and Helmut Muensch

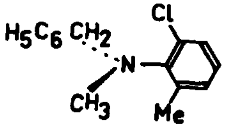
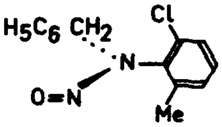
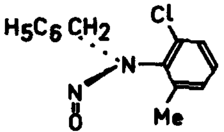
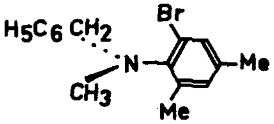
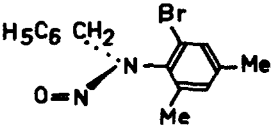
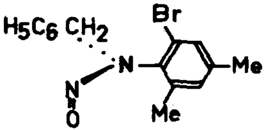
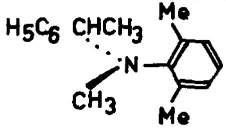
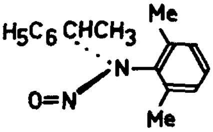
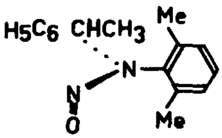
Institut für Organische Chemie, Universität Heidelberg

(Received in UK 3 April 1968; accepted for publication 20 April 1968)

Rotation about the N-aryl bond in anilines is considered to be fast 2). However, a barrier of 15.6 kcal mole^{-1} has recently been reported for N-tert.-butyl-N-benzyl-o-toluidine 3). We have investigated anilines 4) 1, 4, and 7 (see table). The CH_2 protons in 1 and 4 give rise to AB systems in the ^1H-NMR spectra at lower temperatures and to A_2 singlets at higher temperatures 5). Similarly, the different signals for the 2- and 6-methyl groups in 7 are averaged to a singlet when the N-aryl rotation is accelerated. The $\Delta G_c^{\ddagger}$-values obtained can be compared with barriers for the corresponding motion 6) in nitrosamines (see table). In this case cis and trans isomers (referred to the N-N bond) coexist in solution (hexachlorobutadiene, 34°): 59% 2, 41% 3; 60% 5, 40% 6; 11% 8, 89% 9. Such isomers are interconverted very slowly by a process different from N-aryl rotation, as can be seen from the free enthalpies of activation measured by direct cis-trans isomerizations 7) in CCl_4: 23.7 kcal mole^{-1} for 2, 23.5 for 3 (29°); 24.2 for 5, 24.0 for 6 (30.5°); 21.8 for 8, 23.0 for 9 (34°).

The $\Delta G_c^{\ddagger}$-values in the table show that rotation about an N-aryl bond is slowed down in going from an aniline such as 1 through the trans-nitrosamine (e.g. 2) to the cis-nitrosamine (e.g. 3). The rate is also decreased by substitution of chlorine (e.g. in 1) by bromine (resulting in 4) and by increase in the size of substituents on nitrogen.

Hindered rotation about the N-aryl bond in anilinium ions has not been reported. We have studied 10, 11a, 11b, 12a, and 12b by recording the ^1H-NMR spectra of the corresponding anilines 8) in CF_3COOH at 34°. The signals of all CH_2 protons show the expected CH-NH coupling which is absent when CF_3COOD is

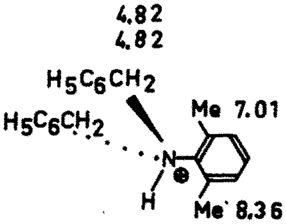
		τ_1 , τ_2	Tc (°C)	$\Delta G_c^{\ddagger}$ (kcal mole^{-1})
1		5.74, 5.95 (−25°)	30	15.1 ± 0.2
2		4.27, 5.76	70	16.5 ± 0.3
3		4.05, 4.87	>127	>20
4		5.73, 5.93 (0°)	43	15.8 ± 0.3
5		4.19, 5.81	99	17.9 ± 0.3
6		4.01, 4.87	165	21.8 ± 0.5
7		7.54, 7.73	63.5	17.6 ± 0.2
8		7.87, 8.42	117	19.8 ± 0.6
9		8.05, 8.78	>140	>21

τ_1, τ_2 : Chemical shifts of CH_AH_B protons (for 1 through 6; J_{AB}= 13.5-14.5 cps) or Me protons (for 7, 8, and 9) at 34°, unless otherwise stated

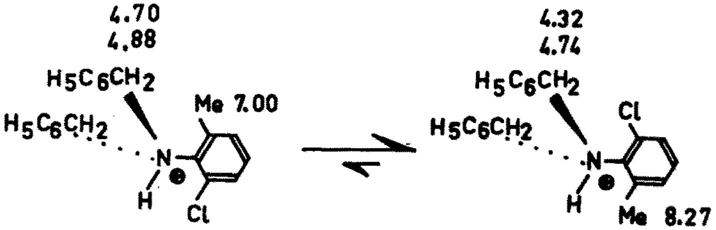
T_c : Coalescence temperature for these absorptions, at 60 Mcps

$\Delta G_c^{\ddagger}$: Free enthalpy of activation at T_c, for N-aryl rotation

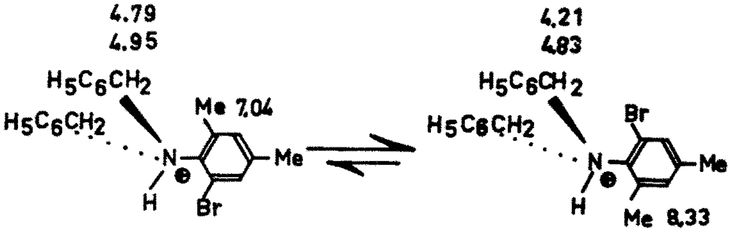
Solvent: Hexachlorobutadiene



10



11a 11b



12a 12b

Figures given with the formulae are τ-values (CF_3COOH)

the solvent. 10 displays four CH_2 protons (which are equivalent by chance) and different 2- and 6-methyl groups. (For chemical shifts see formulae.) This non-equivalence is rationalized by the conformation indicated in the formula (i.e. the hydrogen of the NH group eclipses the benzene ring [9]) or by any similar arrangement differing in rotation about the N-aryl bond by up to 30°. This assumption is consistent with the spectrum of the chloride of ion 10 in $CDCl_3$ at 0° (two methyl singlets at τ = 7.02 and 7.98) and at 50° (average signal at τ = 7.48). 2-Chloro-6-methyl-N.N-dibenzylaniline in CF_3COOD shows two sets of absorptions corresponding to ions 11a (18%) and 11b (82%) each of which gives rise to one AB spectrum for the four CH_2 protons: τ = 4.70 and 4.88, J = 12.8 cps (11a); τ = 4.32 and 4.74, J = 12.6 cps (11b). The two rotamers are correlated with the two sets of absorptions by means of the chemical shifts and the observation that an increase in the size of the halogen atom destabilizes the 2-bromo isomer 12b (59%) with respect to 11b (82%) bearing chlorine in the 2-position. The composition of such equilibria may be useful for the evaluation of steric requirements of substituents, e.g. Me > Br in 12a (41%) and 12b (59%). We cannot exclude with certainty the alternative correlations in which the two benzyl groups enclose the other aromatic ortho-substituent in the otherwise unchanged structures 10, 11a, 11b, 12a, and 12b; our arguments in favour of the correlations given in the formulae will be presented in the full paper. However, this problem does not alter the conclusions drawn above. — Our view is supported by the spectra of **1**, **4**, and **7** in CF_3COOH.

Two mechanisms for methyl interchange in **10** and similar ions are possible: I. rotation about the N-aryl bond in the anilinium ion; II. deprotonation, followed by nitrogen inversion and reprotonation. No matter which of the two processes I and II is faster, both must occur slowly with respect to the NMR time scale when two methyl singlets are recorded. Therefore, it can be concluded from the τ-values (7.01 and 8.36) of the methyl groups in **10** at 34° in CF_3COOH as solvent that $\Delta G_c^{\ddagger}$ for the N-aryl rotation must be greater than 15 kcal $mole^{-1}$.

Experimental assistance by Miss J.Linß and Mrs.G.Rissmann is gratefully acknowledged.

---

1) Part V of the series "Protonenresonanz-Untersuchungen zur inneren Rotation". Part IV: A.Mannschreck and U.Koelle, *Tetrahedron Letters* **1967**, 863. Part III: A.Mannschreck, A.Mattheus, and G.Rissmann, *J.Mol.Spectroscopy* **23**, 15 (1967).

2) J.C.Evans, *Spectrochim.Acta* **16**, 428 (1960). Cf. T.H.Siddall,III, *J.Org.Chem*. **31**, 3719 (1966).

3) B.J.Price, J.A.Eggleston, and I.O.Sutherland, *J.Chem.Soc*. **1967** B, 922.

4) **1**, bp 105-109°(0.01 mm), n_D^{20} 1.5753; **4**, bp 135-140°(0.01 mm), n_D^{24} 1.5850; **7**, bp 100°(0.001 mm), n_D^{22} 1.5589.

5) Similar phenomena in amides are discussed in reference 3), in Y.Shvo, E.C. Taylor, K.Mislow, and M.Raban, *J.Am.Chem.Soc*. **89**, 4910 (1967), in H.Kessler, *Tetrahedron* **24**, 1857 (1968), and in the references cited therein.

6) This motion in a nitrosamine has been demonstrated qualitatively by R.J. Seymour and R.C.Jones, *Tetrahedron Letters* **1967**, 2021 and by T.H.Siddall, III (personal communication).

7) Cf. A.Mannschreck, H.Muensch, and A.Mattheus, *Angew.Chem*. **78**, 751 (1966); *Angew.Chem.Internat.Edit*. **5**, 728 (1966). A.Mannschreck and H.Muensch, *Angew.Chem*. **79**, 1004 (1967); *Angew.Chem.Internat.Edit*. **6**, 984 (1967).

8) N.N-Dibenzylanilines: 2.6-dimethyl-, bp 151°(0.2 mm), n_D^{20} 1.5968; 2-chloro-6-methyl-, bp ~165°(0.25 mm), n_D^{20} 1.6014; 2-bromo-6-methyl-, bp 171-173° (0.1 mm), $n_D^{25.3}$ 1.6077.

9) Cf. G.P.Newsoroff and S.Sternhell, *Tetrahedron Letters* **1967**, 2539.