Hindered Rotation about the N–Aryl Bond in Anilines

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Summary There is a correlation between activation parameters and the steric and electronic effects of the ring substituents in hindered rotation about the N–aryl bond in N-unsubstituted anilines.

HINDERED rotation about the N–aryl bond in anilines has been observed by n.m.r. methods in several compounds, usually sterically hindered compounds with the *ortho*-positions occupied by bulky groups[1] or the nitrogen atom substituted.[1,2] We report the results of an experiment on N-unsubstituted anilines carried out at low temperature with a Varian A-60-A n.m.r. spectrometer, which illustrate the interplay of the conjugation effects.

of the ^{14}N quadrupolar relaxation are weak. The geminal constant J_{H-N-H} could not be determined (in formamide J_{H-H} is about 2·5 Hz).[3]

We believe that the observed phenomena should be attributed to an intramolecular site exchange and not to an intermolecular process which could affect the line shape in the same way. Firstly, the value of ΔG^* is not affected much by the variation of the solvent. Secondly, the work of Rae[4] on the N-methylanilines shows that the proton exchange varies with the pK_a of the compound; at ordinary temperatures it is slow for all the nitro-substituted anilines and, moreover, it is very much reduced in a basic solvent. In addition, we observe a new widening of the line at about

TABLE

Aniline					pK_a (20 °C)	δ (NH$_2$)	T_c	$\Delta G^*(T_c)$	ΔH^*
(I)	2-Chloro-4-nitro	..	..	..	18·06	6·75	212	10·2	
(II)	4-Chloro-2-nitro	..	..	..	18·34	7·45	201·5	10·6	15
(III)	2,4-Dinitro	..	..	..	15·51	8·40	229	12·2	
(IV)	2,4-Dichloro-6-nitro ..	..	..	16·39	7·28	205	9·9	9·0
(V)	2-Bromo-4,6-dinitro ..	..	..	12·80	7·95	245	12	13·7

T_c: coalescence temperature of NH lines (± 3 K) (in acetone).
$\Delta G^*(T_c)$: free enthalpy of activation ($\pm 0·2$ kcal/mol) (in acetone).
ΔH^*: enthalpy of activation (± 2 kcalfimol) (in acetone).
δ (NH$_2$): chemical shifts in (Me$_2$SO) ($\pm 0·10 \times 10^{-6}$).

The results are shown in the Table. Chemical shifts were determined in pure dimethyl sulphoxide and the pK_a values measured in water–Me$_2$SO mixture (95·5% Me$_2$SO). Acetone was used as a solvent at low temperature. Two NH lines were observed in the low-temperature spectrum; the coalescence temperatures were between 200 and 245 K. No substantial variations of line width [in (I) and (II)] were observed at 200 K (very slow exchange rates) or at 270 K (fast exchange rates); it therefore seems that the variations

290 K, then a progressive disappearance of the signal. In hexachloroacetone an absorption reappears at about 450 K. The observed facts are attributed to an intermolecular exchange (impurities of the solvent or of the solute.).

A study of the results reveals the following points: (i) the pK_a and δ_{NH} values seem to correlate with the activation parameters for a given class of compounds (di- or tri-substituted); (ii) with increasing steric hindrance (II → IV or III → V) the values of ΔG^* and ΔH^* decrease

and δ_{NH} shifts to high fields (the energy content of the ground state increases and the energy difference for passing to the transition state becomes smaller); (iii) replacement of 4-chloro by 4-nitro gives rise to an increase in the value of ΔG^* (II) and III), in keeping with increasing σ constants from the compilation of Hine[5] or Taft;[6] (iv) comparison between (I) and (III) illustrates the role of an *ortho*-NO_2 group likely to form a hydrogen bond with an amino-portion and thus to stabilize the planarity of the system.

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