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SOLVENT EFFECTS IN NMR SPECTRA INDUCED BY AROMATIC AMINES IN NITROALKANES

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Polarographic studies (1) on nitroalkanes in aromatic amines have shown that no ionization of the nitroalkanes takes place at all. In order to confirm this evidence the present work was undertaken.

The proton magnetic resonance spectra (2) of sodium salts of nitroalkanes exhibit a large paramagnetic shift, as compared to nitroalkanes, which is due to the olefinic bond of nitro anions. However, the proton magnetic resonance spectra (Table 1) of dilute solutions of nitromethane, nitroethane, nitropropane and nitroisopropane in aromatic amines, like aniline, dimethylaniline, o-toluidine and o-chloroaniline, but unlike nitro anions, exhibit a large diamagnetic shift, as compared to nitroalkanes in CCl_4 ($\delta_{CCl_4} - \delta_{C_6H_5NH_2}$ = 60 - 30 cps). This shift is a typical aromatic solvent shielding effect (3) and it is not due to the amino group, since the nmr spectra of nitroalkanes in aliphatic amines show a small paramagnetic shift ($\delta_{CCl_4} - \delta_{n\text{-}PrNH_2} \simeq -8$ cps). The observed diamagnetic shielding effect is decreased from nitromethane to nitroethane and nitropropanes, and on the other hand it is increased with increasing π-electron density of the aromatic ring.

It is well known (4,5) that nmr solvent shifts induced by aromatic solvents can be used for the solution of several configurational problems. Assuming that the diamagnetic shift of nitroalkanes in aromatic amines is mainly due to a 1:1 collision complex, as recently proposed (4,6) for the explanation of solvent effects in nmr spectra, then in the case of nitroethane-aniline mixtures a "parallel-type" (7) complex should be formed, with the C-C axis of the nitroethane molecule parallel to the plane of the associated aromatic ring (Fig. 1), since the diamagnetic shift of the methyl group is the same as that of the methylene ($\delta_{CCl_4} - \delta_{C_6H_5NH_2}$ = 42 cps). It is of interest to note that an analogous structure has been proposed (4,7) for the nitrobenzene-benzene complex.

The assumption of formation of a 1:1 collision complex is supported by spectrophotometric examination of the mixture nitroethane-aniline. Thus, the ultraviolet-visible spectrum of nitroethane in aniline showed a weak absorption at 370 mμ and spectrophotometric study based on the continuous variation method supports the suggestion of a 1:1 complex formation.

Table 1

NMR absorptions of nitroalkanes in cps downfield from TMS in 2% w/v solutions

Compound	Absorption	Solvent				
		CCl_4	$C_6H_5NH_2$	$C_6H_5N(CH_3)_2$	$C_6H_4NH_2CH_3$(-o)	$C_6H_4NH_2Cl$(-o)
CH_3NO_2	CH_3	258	~203*	197	203	220
$CH_3CH_2NO_2$	CH_3	95	53	51	52	62
	CH_2	262	220	211	217	*
$CH_3\overset{2}{C}H_2\overset{1}{C}H_2NO_2$	CH_3	63	31	30	31	36
	CH_2-2	122	84	82	82	93
	CH_2-1	258	220	212	~217*	*
$(CH_3)_2CHNO_2$	CH_3	93	59	57	58	66
	CH	274	236	230	234	*

* It is masked by the solvent peak.

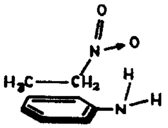

Fig. 1

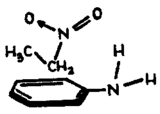

Fig. 2

In the case of the nitroethane-dimethylaniline complex the diamagnetic shielding of the methylene group is more effective ($\delta_{CCl_4} - \delta_{C_6H_5N(CH_3)_2}$ = 51 cps) than that of the methyl ($\delta_{CCl_4} - \delta_{C_6H_5N(CH_3)_2}$ = 44 cps) and this fact can be explained either by assuming that the C-C axis of nitroethane is inclined to the plane of aromatic ring, or that the nitroethane molecule, because of steric interaction of the dimethylamino and nitro groups, is shifted parallel to the plane of the ring, so that the methyl group is less shielded than the methylene. The existence of steric interaction in the complex indicates that the C-C axis of nitroethane rather lies in a parallel position to the C-N axis of aromatic amine and probably in cis-position in respect to the relative position of nitro and amino groups (Fig.1), although the perpendicular one (Fig. 2), as more symmetric, should better explain the same shielding of methyl and methylene group in aniline complex. However, the difference in diamagnetic shielding of methyl and methylene groups in asymmetric amines, like as o-toluidine, is not more than 2 cps. This fact suggests that the asymmetry caused by a parallel position of the nitroethane molecule with respect to the C-N bond of aniline does not have any appreciable effect on the diamagnetic shift of methyl and methylene group.

In the nitropropane-aniline complex the methylene groups have nearly the same location relative to aromatic ring and are then shielded to the same extent ($\delta_{CCl_4} - \delta_{C_6H_5NH_2} = 38$ cps), but the methyl group is located further from the center of the ring and is then less shielded ($\delta_{CCl_4} - \delta_{C_6H_5NH_2} = 32$ cps).

In the case of the nitroisopropane-aniline complex the methine hydrogen lies in a perpendicular position to the plane of the aromatic ring ($\delta_{CCl_4} - \delta_{C_6H_5NH_2} = 38$ cps), whereas the two methyl groups are symmetrically located around the methine hydrogen and are less shielded. Their position relative to the aromatic ring should be similar to that of methyl group in nitropropane, since both show almost the same diamagnetic shift ($\delta_{CCl_4} - \delta_{C_6H_5NH_2} =$ 34 - 32 cps).

Analogous structures are proposed for the complexes of nitroalkanes with the other amines.

The nmr spectra were obtained with a Varian Associates A60A spectrometer at normal probe temperature (~ 40°) and with TMS as internal standard. The nitroalkanes used were obtained from Ferak Chemicalien, p.a., and their chemical shifts in CCl_4 (see Table 1) were in agreement with those of the literature (8). The amines, puriss, were obtained from Fluka AG. Two independent measurements were made on each compound. The spectrophotometric measurements were obtained with a Perkin-Elmer 137 UV spectrophotometer with 0.5 cm path cells. The condinuous variation method was made at 370 mμ with 2N solutions of nitroethane and aniline in CCl_4. As reference an aniline solution in CCl_4, of the appropriate concentration in order to balance the absorption of aniline in the sample beam, was used.

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