Solvent Effect on Hydrogen Bonding in *ortho*-Nitroanilines

By V. BEKÁREK,* J. KAVÁLEK, J. SOCHA, and S. ANDRÝSEK

(*Department of Organic Chemistry, Institute of Chemical Technology, Pardubice, Czechoslovakia*)

THE EXISTENCE of intramolecular hydrogen bonding in *o*-nitroanilines in deuteriochloroform solution and its disappearance in dimethyl sulphoxide solution has recently been supported by n.m.r. studies of the aromatic protons of these compounds.[1] The foregoing study of this problem[2] which rested on solvent-shift studies of i.r. spectra has also given some evidence contrary to the suggested intramolecular hydrogen bonding even in non-basic solvents.

We now present further evidence about the existence of the intramolecular hydrogen bond in *o*-nitroanilines in solution in deuteriochloroform and its disruption in dimethyl sulphoxide solution by means of the dependence of the chemical shift of amino-protons (τ_{NH_2}) on Hammett substituent constants (σ) in substituted *o*-nitroanilines. For correlation of the chemical shift of intramolecular hydrogen-bonded protons in aromatic systems we recently proposed equation (1)[3]

$$\tau = \tau_0 + b\sigma_1 + c\sigma_2 \qquad (1)$$

where term $b\sigma_1$ expresses the effect of the substituents *via* the N–H bond (σ_1 of the substituents is considered with regard to NH_2 group) and term $c\sigma_2$ expresses the effect on the chemical shift *via*

Comparison of the experimental and calculated values of the chemical shifts of the amino-protons of o-*nitroanilines in deuteriochloroform and dimethyl sulphoxide solutions.*

Substituent	σ_1	σ_2	τ_{NH_2} ($CDCl_3$) Exp.	Calc.	τ_{HN_2} (Me_2SO) Exp.	Calc.
4-OMe	−0·268	0·115	3·99	3·99	2·95	2·95
5-NMe_2	−0·211	−0·600	3·75	3·75	2·92	2·93
-H	0·000	0·000	3·85	3·85	2·82	2·82
4-F	0·062	0·337	3·94	3·93	2·79	2·79
4-Cl	0·227	0·373	3·85	3·87	2·66	2·71
4-Br	0·233	0·391	3·85	3·87	2·66	2·70
4-I	0·276	0·352	3·84	3·84	2·66	2·68
5-Cl	0·373	0·227	3·77	3·76	2·65	2·63

the electron donor in the intramolecular hydrogen bond (in this case the NO_2 group; σ_2 of the substituents is considered with regard to this group). The first effect is similar to that observed in anilines and phenols,[4] but the second effect is reversed, *i.e.* the substituents with a higher σ constant weaken the hydrogen bonding (decreased electron density on the electron donor) and, accordingly, shift the values of τ_{NH_2} to higher fields, while the substituents with a lower value of σ strengthen the hydrogen bonding (increase in the electron density on the electron donor) and shift the value of τ_{NH_2} to lower fields. The equation (1) has the form $\tau = 3·85 - 0·414\sigma_1 + 0·300\sigma_2$ (solutions in $CDCl_3$ at 0°), or $\tau = 2·82 - 0·500\sigma_1 - 0·025\sigma_2$ (solutions in Me_2SO at 20°) for the systems *o*-nitroanilines in deuteriochloroform and dimethyl sulphoxide. The significant value of the constant *c* in the case of the deuteriochloroform solutions, and its negligible value in the case of the dimethyl sulphoxide solutions (< experimental error of 0·015 p.p.m.) point to the existence of the intramolecular hydrogen bond in *o*-nitroanilines in deuteriochloroform solutions and its absence in dimethyl sulphoxide solutions.

(*Received, April 2nd,* 1968; *Com.* 409.)

[1] I. D. Rae, *Chem. Comm.*, 1966, 519.

[2] L. K. Dyall and J. E. Kemp, *Spectrochim. Acta*, 1966, **22**, 467, and references cited.

[3] V. Bekárek, J. Socha, and M. Večeřa, *Coll. Czech. Chem. Comm.*, in the press.

[4] V. Bekárek, J. Klicnar, F. Kristek, and M. Večeřa, *Coll. Czech. Chem. Comm.*, in the press.