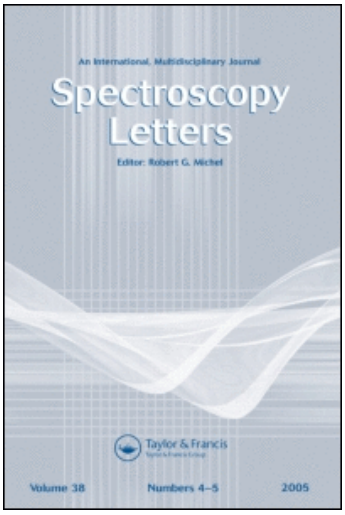

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Spectroscopic Studies of Some Organic Compounds: Solvent Effects on ^{1}H NMR Shift of Amine Proton of Morpholine

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Spectroscopic Studies Of Some Organic Compounds: Solvent Effects On ^{1}H NMR Shift Of Amine Proton Of Morpholine.

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Abstract:

The influence of the aprotic solvents on the ^{1}H NMR spectra of the N-H proton has been studied. The chemical shift shows quite good correlation with the solvatochromic parameters, π^{*}, β, and α, while a fair correlation with the Gutmann donor and acceptor numbers were obtained.

Introduction:

Solvent polarity and hydrogen bongding effects on a number of physical and chemical properties and reaction

parameters are unravelled and rationalized by mean of the Solvatochromic equation[1-5], of a general form:

$$XYZ = XYZ_0 + s(\pi^* + d\,\delta) + a\alpha + b\beta \quad \ldots.(1)$$

The π^* - scale of dipolarity-polarizabilities[1] describes the ability of a solvent to stabilize a solute charge or dipole by virtue of it's dielectric effect; The α - scale of hydrogen bond donor (HBD) acidities[4], measure the solvent ability to share a proton in a solvent-to-solute hydrogen bond; The β -scale of hydrogen bond accepter (HBA) basicities[4], measure the solvent ability to share a proton from an hydrogen bond donor solute. δ -is a polarizability correction term equal to (0.0) for non-chlorinated aliphatic solvents, (0.5) for polychlorinated aliphatic and (1.0) for aromatic solvents; s, d, a, and b - represent the responses of XYZ to the solvents polarity, polarizability and hydrogen bonding properties. The XYZ term in equation (1) may be the Logarithm of a rate constant, equilibrium constant, the position or intensity of maximal absorption in an IR, UV, NMR, or ESR spectrum...etc.

Correlation of these type has been the subject of extensive study which was so far reported include, bathochromic shift attributable to hydrogen bonding in U.V-Visible spectra of a large number of aniline and phanol derivatives[2,3]. ^1H NMR hydrogen bonding shifts of fluorodinitromethane, 3-methylbut-3-en-1-yne and chloroform[4]; IR streching frequency shifts of phenol and 4-fluorophenol[6].

Table (1): ^{1}H NMR Spectral Shift of N-H proton of morpholine and solvents parameter[a] used for multiple linear correlations.

Solvent	δ at 10%	δ at 40%	π^*	α	β	DN	AN
Dioxane	2.20	2.35	0.55	0	0.37	14.8	10.8
Pyridine	2.50	2.45	0.87	0	0.64	33.1	14.2
Acetone	2.30	2.35	0.71	0.07	0.48	17.0	12.5
Acetonitral	2.20	2.21	0.76	0.24	0.31	14.1	18.9
Nitrome-thane	2.20	2.17	0.8	0.31	0.2	2.7	20.5
DMF	2.68	2.48	0.88	0	0.7	26.6	16.0
DMSO	2.90	2.4	1.0	0	0.76	29.8	19.3
PhH	1.35	1.68	0.59	0	0.1	0.1	8.2
PhMe	1.30	1.8	0.54	0	0.11	0.1	-
PhOMe	1.60	2.1	0.73	0	0.22	-	-
PhBr	1.48	1.91	0.79	0	0.06	-	-
PhCl	1.5	2.0	0.7	0	0.07	-	-
$CHCl_3$	1.95	2.10	0.76	0.38	0	4.0	23.1
CH_2Cl_2	1.95	2.26	0.8	0.3	0	-	20.4

a- values taken from references cited in text.

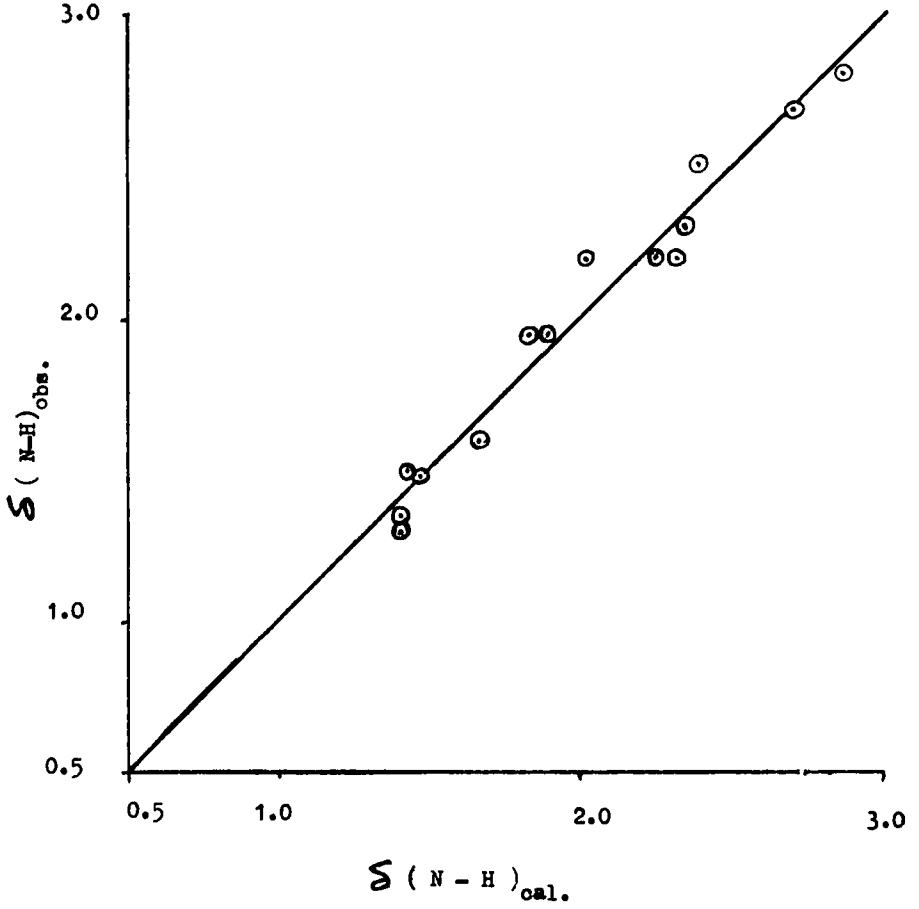

Fig.: Plot of δ(N-H) observed VS. δ(N-H) calculated according to equation (4).

In similar vein Gutmann[7] has developed other parameters for solvent nucleophilicity and electrophilicity known as donor number (DN) and acceptor number (AN), which have been proposed to unravel some of the different properties of the medium.

The present work is concerned with the application of multi-parameter equations to resolve solvent effects on the ^1H NMR spectra of the N-H proton of morpholine at 10% and 40% concentration V:V.

Result and Discussion:

The chemical shifts of N-H proton of morpholine observed using TMS as internal reference are assembled in table (1) to gether with the solvents parameters.

The correlation of our result in table (1) with singl solvents parameter was poor with a correlation cofficient ($r \leqslant 0.7$).

The correlation was improved by the multi-solvent parameter treatment which implicitly allows for various independent interaction mechanism between solvent and solute, since it transpires that no single parameter can deal effectively with all of the type of phenomenon which vary with solvent.

The first set of parameter analysis by stepwis regression was solvatochromic parameters:

$$\delta \text{ N-H} = 1.052 + 1.740\ (\pi^* - 0.4\,\delta) \pm 0.24 \quad \ldots\ (2)$$

$$n = 14,\ C.F^{**} = 0.1\ ,\ r = 0.81$$

** C.F = critical F. value

$$\delta_{N-H} = 1.107 + 1.170\,(\pi^{*} - 0.4\,\delta) \pm 0.183 + 0.898\,\beta \pm 0.18 \quad \ldots\ldots (3)$$

$n = 14,\ C.F = 0.1,\ r = 0.94$

$$\delta_{N-H} = 1.152 + 0.578\,(\pi^{*} - 0.4\,\delta) \pm 0.25 + 1.516\,\beta \pm 0.25 + 1.111\,\alpha \pm 0.38 \quad \ldots\ldots\ldots (4)$$

$n = 14,\ C.F = 0.1,\ r = 0.97$

The goodness of the statistical fit increases significantly in the multiple linear regression equation with β and α (eq. 2-4). The b/s ratio equal (2.61) in equation (4) suggests that the solvents basicity parameter (β) effects account for significant proportion of the total shift. While acidity parameter (α) shows a fair improvement in the correlation (eq. 2-4) indicates the minor dependences of the chemical shift on solvents acidity. The a/s ratio equal (1.92) smaller value than b/s ratio supports the preferment of basicity parameter on the chemical shift.

On the other hand a poor correlation was obtained when a chemical shift values measured at 40% V:V was introduced in regression. (equation 5).

$$\delta_{N-H} = 1.862 + 0.088(\pi^{*} - 0.4\,\delta) \pm 0.35 + 0.715\,\beta \pm 0.36 + 0.568\,\alpha \pm 0.55 \quad \ldots\ldots (5)$$

$n = 14,\ C.F = 0.1,\ r = 0.7$

Poorer quality correlation obtained at high concentration as might be expected due to large self association effect compared with the solvation effect.

The next set of equations (6,7) involves the Gutmann donor number (DN), and accepter number (AN). Avalues are available for only nine solvents (table 1).

$$\delta_{N-H} = 1.761 + 0.0311DN \pm 0.007 \quad \text{..... (6)}$$
$$n = 9,\ C.F = 0.1,\ r = 0.72$$

$$\delta_{N-H} = 1.213 + 0.0314DN \pm 0.005 + 0.034AN \pm 0.013 \quad \text{.....(7)}$$
$$n = 9,\ C.F = 0.1,\ r = 0.86$$

There is arelatively fair linear relationship between the chemical shifts of the N-H proton and the donor number for the solvents. This is interpreted as aresult of a solute-solvent interaction due to the nucleophilic attack of the solvent at the N-H proton. The greater down field shift induced by more basic solvents, (table 1).

Conclusion:

Although there is no critical definition available for the conditions under which each parameter must be used, it seems that the best approach to understand the solvent effects on the N-H shift is primarily in terms of nucleophilicity (basicity) and solvent dipolarity - polariza-

bility as a major and in term of electrophilicity (acidity) as a minor.

Experimental:

The ^{1}H NMR measurements were carred out on 60 MHz Hitachi Perkin-Elmer R-24 spectrometer at 25C°. The chemical shifts were determined using tetramethylsilane (TMS) as internal reference. Morpholine was purified by standard method[8] then fractionally distilled, middle fraction was kept in a dark bottol, and used for this study.

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