Solvent Effect on the Si-O Stretching Bands of Benzilidene (ortho Dimethylhydrogenosiloxy) Aniline by IR Spectroscopy

M. MAZHAR*, SAQIB ALI, M. JAVID, M. IKRAM AND M. IRSHAD ZIA
Department of Chemistry, Quaid-e-Azam University, Islamabad, Pakistan

Summary: The effect of solvent-solute interaction on vibrational spectra of benzilidene (o-dimethylhydrogenosiloxy) aniline was studied in a number of solvents. The spectral vibrational frequency shifts observed in different solvents have been correlated with refractive indexes and dielectric constants of the solvents. The results obtained were applied to the Buckingham's modification of the Bauer-Magat formula for solute-solvent interaction. Generally, infrared spectral frequencies of Si-O bands in solution phase shifted to lower wavenumber than those observed in gas phase, except in nitrobenzene which is attributed to specific interaction. The calibration lines between $\Delta v/v$ vs $\varepsilon-1/2\varepsilon+1$ were made to determine the specific and non specific solute-solvent interactions. Results obtained from these calibration lines are also discussed in terms of solute-solvent interactions.

Introduction

The infrared spectra recorded in solvents of different polarity show that the position, intensity and shape of absorption bands are usually modified by these solvents [1-2]. These changes are a result of physical intermolecular solute-solvent interactions such as weak nonspecific interactions (dipole-dipole, dipole-induced dipole, etc.) and strong specific association of solute with solvent molecules, usually of hydrogen bond type [3].

Solvent induced frequency shifts have been intensively studied since the initial application of Onsager's theory [4]. However, the studies have been restricted to localized vibration of pure organic compounds [5-8]. Silicon compounds are of interest because of their varying capability of bond formation. In this respect their vibrational frequencies with different groups will show varying behavior in many solvents. In an attempt to extend

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*To whom all correspondence should be addressed.

the work on substituted compounds, we have studied the effect of solvent behavior on Si-O stretching bands in benzilidene and interpret the data in terms of specific and nonspecific interactions.

Results and Discussion

Infrared characteristic group frequencies of benzilidene (o-dimethylhydrogenosiloxy) aniline in thin film, gas phase and various solvents i.e. carbon tetrachloride, benzene, chloroform, acetone and nitrobenzene were recorded as shown in Fig. 1. The relative shift in frequencies ($\Delta v/v$) of various infrared bands of the compound in various solvents are given in Table-1. The vibrational spectra of benzilidene (o-dimethylhydrogenosiloxy) aniline in various solvents show variation in the shape, frequency and intensity of the bands which may be due to interaction of solute with the solvent molecule. The change in half width $v_{1/2}$ of Si-O bands in various solvents are given below:

vapour phase	40 cm^{-1}
Carbon tetrachloride (CCl$_4$)	23 cm^{-1}
Benzene (C$_6$H$_6$)	19 cm^{-1}
Chloroform (CHCl$_3$)	25 cm^{-1}
Acetone (CH$_3$COCH$_3$)	17 cm^{-1}
Nitrobenzene (C$_6$H$_5$NO$_2$)	38 cm^{-1}

Table-1: Dielectric constants, refractive index and relative shift of vibrational frequencies of various bands of the compound in a number of solvents.

	CCl$_4$	C$_6$H$_6$	CHCl$_3$	CH$_3$COCH$_3$	C$_6$H$_5$NO$_2$
ε(25°C)*	2.228	2.274	4.806	20.7	34.38
n*	1.4630	1.5011	1.4457	1.3591	1.5524
$\Delta v/v$ of vsym (Si-O)	0.022	0.025	0.033	0.033	0.030

*Taken from Ref. 12.

On the basis of half width $v_{1/2}$ values, interaction of solvent with solute can be categorized as weak, medium and strong.

In case of benzene and acetone, weak interactions appear as the peaks are sharp with smaller widths, indicating that Si-O vibrations are not perturbating greatly and weak interactions with these bands occur.

In chloroform, the values of half band widths are somewhat larger, thus indicating that this solvent has medium weak interacting nature for benzilidene (o-dimethylhydrogenosiloxy) aniline.
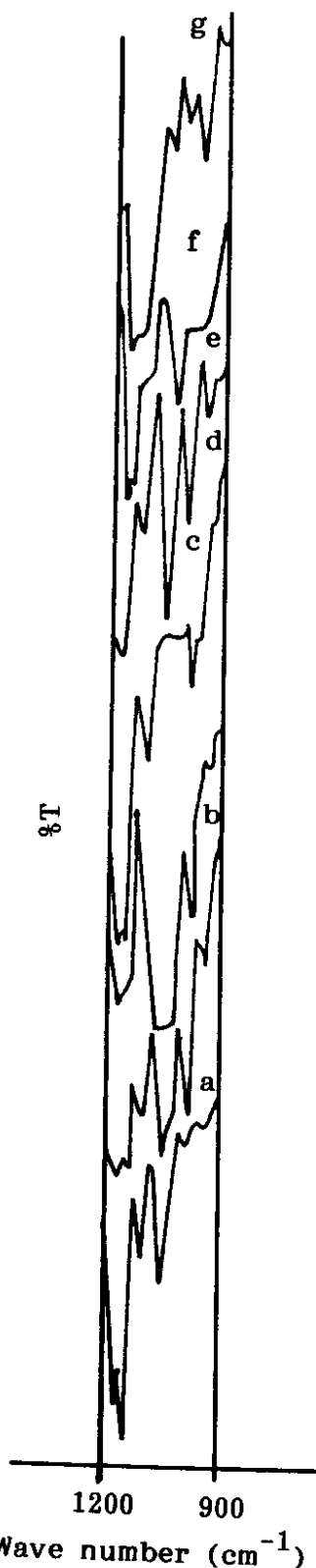

%T

1200   900

Wave number (cm^{-1})

Fig. 1: Si-O vibration rang in (a) gas phase (b) thin film (c) CCl$_4$ (d) CHCl$_3$ (e) (CH$_3$)$_2$CO (f) C$_6$H$_5$NO$_2$ and (g) C$_6$H$_6$.

In nitrobenzene, the half band width value is larger, which can be assigned to very weak specific interactions or strong non-specific interaction [5].

This behaviour of solvents can be supported by KBM line for Si-O band of the compound. The plot of $\Delta v/v$ vs $\varepsilon-1/2\varepsilon+1$ drawn by least square method is shown in Fig. 2. Here again, CCl_4, $CHCl_3$ and nitrobenzene show deviation from the line, showing relatively strong interaction with the solute. The vapour frequency point is of course at the origin [9], since the relative shift is zero and $\varepsilon-1/2\varepsilon+1$ factor for vapour is also zero (ε for varpour is approximately unity).
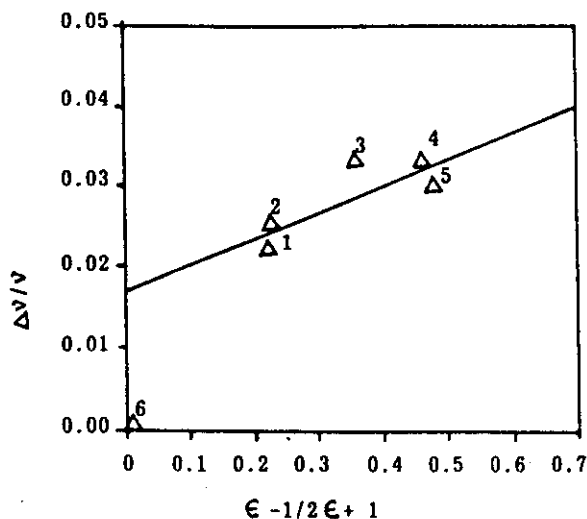

Fig. 2: $\Delta v/v$ vs $\varepsilon-1/2\varepsilon + 1$ for stretching mode of Si-O band in solvent (1) CCl_4 (2) C_6H_6 (3) $CHCl_3$, (4) $(CH_3)_2CO$ (5) $C_6H_5NO_2$ (6) varpour phase.

Backingham's [10] equations for polar and non-polar solvent respectively are:

$$\Delta v/v = C_\alpha + C_\varepsilon (\varepsilon-1/2\varepsilon+1) + C_n (n^2 - 1/2n^2 + 1) \quad (1)$$

$$\Delta v/v = C_b + 1/2 (C_\varepsilon+C_n) (\varepsilon-1/2\varepsilon+1) \quad (2)$$

Where C_ε and C_n are constants for solute under consideration. If we eliminate C_ε an expression is obtained for polar solvents [7].

$$\Delta v/v = C + C_n (\varepsilon-1/2\varepsilon+1 - n^2-1/2n^2 + 1) \quad (3)$$

From the intercept of KBM plot $\Delta v/v$ vs ($\varepsilon-1/2\varepsilon + 1$) value obtained for Ca = 0.01697 for Si-O vibration. From equations 1 and 3, using shifts in polar solvents (acetone), values obtained for $C_n = 0.0564$ and $C = 0.01298$. The direct value of the slope from the graph is 0.03311 which is comparable with the slope equal to 0.03469 found from equation 3. The value of intercept from the graph is 0.01697 which is comparable with intercept (C_b) equal to 0.017035 found from equation 3 using shift in non-polar solvent (C_6H_6). Hence it is clear that weak interactions which are non-specific seems to be supported by the experiment. This interpretation is in agreement with already reported in the literature [11] for non-specific model.

The deviation of nitrobenzene, CCl_4 and $CHCl_3$ from the KBM plot for Si-O band may be due to weak specific interaction which can be characterized by features such as IR stretching mode of vibration shifting towards lower frequency and broadening of the peak.

Experimental

The infrared spectra were recorded on a Hitachi model 270-50 infrared double beam spectrophotometer using KBr cells of thickness 0.1 mm. The concentration of solutions were 0.2% v/v ($1.6 \times 10^{-2}M$), 0.4% v/v ($3.9 \times 10^{-2}M$), 1% v/v ($8.24 \times 10^{-2}M$) and 2% v/v ($16.48 \times 10^{-2}M$). Fundamental frequencies were measured using Merck Schuchardt spectroscopic grade solvents without further purification.

Benzilidene (o-dimthylhydrogenosiloxy) aniline was prepared as follows:

To a solution of 9.00 gms (0.05 mole) of benzilidene aniline and 5.0 gms (0.05 mole) of Et_3N in 300 cm^3 ether in a two neck flask fitted with a reflux condenser, was added dropwise a solution of 4.73 gms (0.05 mole) of $(CH_3)_2Si(H)Cl$ in 50 cm^3 ether from a dropping funnel at 100m temperature with constant stirring. Immediately a white suspension was formed. The reaction mixture was stirred overnight and filtered. The filtrate was evaporated to give a thick syrupy liquid which on distillation at 125-130°C/0.3 mbar gave 3.4 g 35%

yield. Found C: 70.72; H: 6.44; N: 5.40 $C_{15}H_{17}NOSi$ requires C: 70.31; H: 6.64; N: 5.46.

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