

Substituent Effect on the infrared spectra of Unsymmetrical Azines

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Abstract:

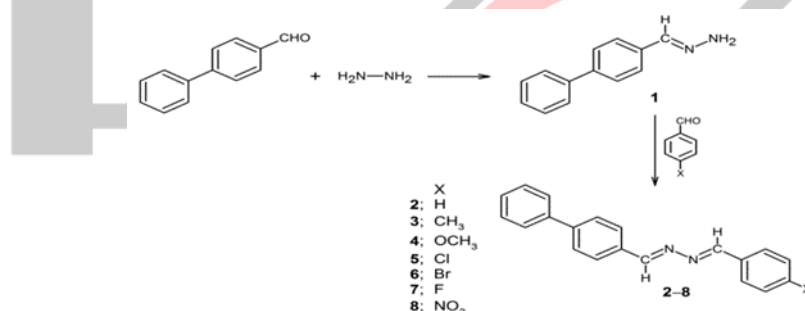
A series of novel unsymmetrical azines are prepared [1] and characterized by FT-IR, ^1H , ^{13}C NMR, Mass and UV spectral studies and their IR, are recorded. The effect of substituent on $>\text{C}=\text{N}$ and $\text{N}-\text{N}$ stretching frequency were studied. The correlation of IR frequency with Hammett substituent constants are not fair enough, σI and σR parameters give fair correlations. Uniformly σI and σR parameters collectively explain substituent effect.

INTRODUCTION

Azines, condensation products of hydrazine and carbonyl compounds are designated as symmetrical or asymmetrical azines, based on the two carbonyl compounds from which the azine derived are the same or different. Azines are both chemically and biologically important molecules with potent physical properties [2–9]. Azines with donor and acceptor groups at the ends of p -conjugated backbone behave as novel nonlinear optical (NLO) materials. This property of azine is attributed to the development of light based technologies for communication and computing [11]. Only a limited work has been reported in the synthesis and biological aspects of azines derived from several hetero aromatic and bicyclic carbonyl compounds. The present investigation is focussed on the effect of substituents on the infrared frequencies [12–14] in several Unsymmetrical azines. A very substantial amount of data are available on $>\text{N}-\text{N}$ and $\text{C}=\text{N}$ -stretching frequencies in open chain systems. Their use in structure parameter correlations have now become very popular. A similar study involving Azines is utmost unknown. Hence, several para-substituted Azines were prepared and their infrared spectra were recorded with a view to study the structure parameters correlations in these Azines.

MATERIALS AND METHODS

About 0.01 mol of 4-biphenylcarboxaldehyde and 5 mL of hydrazine hydrate (0.01 mol) was taken in a stoppered conical flask. To this mixture few drops of acetic acid was added. The reaction mixture was stirred well for about half an hour. The hydrazine was separated as white solid and it was stirred with benzaldehyde (0.005 mol). The mixture was cooled. Yellow solid separated out and it was filtered, washed and recrystallized from ethanol. The other unsymmetrical azines 3–8 are synthesized in the similar manner.



RESULTS AND DISCUSSION

IR SPECTRA

FT-IR spectral studies of 2–8 The sharp peaks around 1600 cm^{-1} in the FT-IR spectra are exhibited to $\nu\text{C}=\text{N}$ mode. Aromatic $\text{C}=\text{C}$ stretching vibrations are seen around 1500 and 1450 cm^{-1} . The peaks around $1069\text{--}1005\text{ cm}^{-1}$ are due to the $\text{N}-\text{N}$ stretching mode. Aromatic $\text{C}-\text{H}$ out-of-plane bending vibrations appeared around 840 and 757 cm^{-1} . Two very strong adsorption bands at 1515 and 1337 cm^{-1} in the FT-IR spectrum of unsymmetrical azine 8 are attributed to antisymmetric and symmetric NO_2 stretching vibrations respectively. Asymmetric bending vibration for methyl group appeared at 1300 cm^{-1} for azine 3. FT-IR spectral data of 2–8 are listed in Table 1.

Effect of substituents on $\text{C}=\text{N}$ and $\text{N}-\text{N}$ stretching frequency

Normally Azines show two carbonyl bands for S -cis and S -trans conformers in solution. Although an equilibrium mixture of different conformations of some of the Azines may exist in crystalline state. In addition to $\text{C}=\text{N}$ the system under investigation also shows strong band due to the $\text{N}-\text{N}$ group that is present in the system.

The C=N stretching frequencies of these Unsymmetrical azines shows that the lowest C=N frequency is observed. When a powerful electron donating group is present. This may be due to the fact that electron donating group reduces the double bond character of the C=N band and thereby lower the frequency. The increase in C=N absorption frequency is attributed to the loss of co-planarity of substituent with the C=N. The IR spectral values are given in Table(1)

Table-1. C=N and >N-N stretching frequencies of substituted Unsymmetrical azines

Substituent	Assignment ν (cm^{-1})	
	C=N	N-N
H	1628	1005
p-CH ₃	1620	1175
p-OCH ₃	1617	1170
p-Cl	1630	1089
p-Br	1631	1069
p-F	1634	1153
p-NO ₂	1643	1185

The data which are given in the Table-1 are separately analysed through various correlation equations involving σ and σ^+ values Fig(1-2). The results of statistical analysis are presented in Table -2

Table-2 Results of statistical analysis of C=N and >N-N stretching frequencies of Unsymmetrical azines

System	Constant for correlation	A	B	S.D	R	substituents
$\nu_{\text{X=N}}(\nu_{\mu})$	σ	1630	4.4017	2.9463	0.464	H, p-CH ₃ , p-Cl, p-OCH ₃ , p-F, p-Br, p-NO ₂
	σ^+	1631	2.340	3.0786	0.381	
$\nu_{>\text{N-N}}(\nu_{\mu})$	σ	1050	-30.95	28.080	0.370	
	σ^+	1055	-26.06	25.35	0.498	

A = Intercept; B = Slope

All the correlation data given in Table -2 are pertaining to single parameter equation which indicates clearly that poor correlation is obtained with Hammett σ and σ^+ constants. The single parameter correlations are shown in Figs. 1-2. In view of the inability of some sigma constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlation involving ρ_I and ρ_R constants. The correlation equations generated are shown in **Table-3 Correlation equation with ρ_I and ρ_R constants.**

System	Correlation equation in $\nu_{\text{C=N}}(\text{cm}^{-1})$	Substituent
Unsymmetrical azines	$\nu_{\text{X=O}} = 1616.96 + 5.67 \rho_I + 6.44 \rho_P$ (P = 0.743, $\Sigma \Delta = 2.255$, $\nu = 8$)	H, p-CH ₃ , p-Cl, p-OCH ₃ , p-F, p-Br, p-NO ₂
	$\nu_{>\text{N-H}} = 1056.62 - 4.4813 \rho_I - 53.4705 \rho_P$ (P = 0.492, $\Sigma \Delta = 28.14$, $\nu = 8$)	

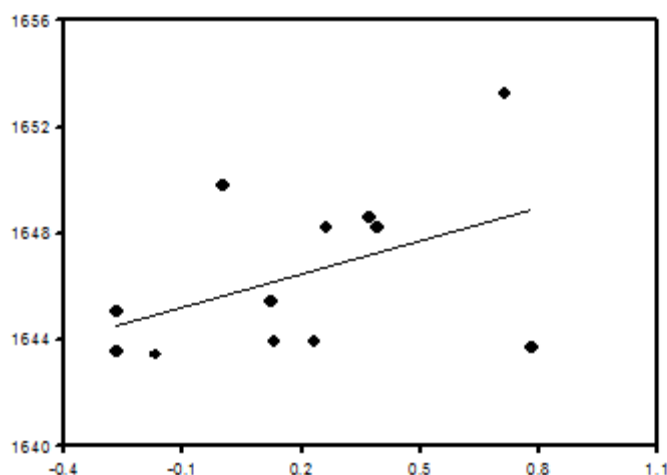


Fig. 1. Plot of $\nu_{C=O}$ (cm^{-1}) substituted Azines versus σ

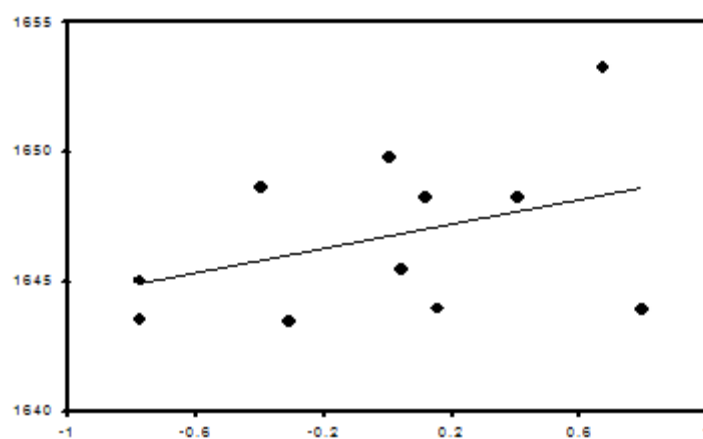


Fig. 2. Plot of $\nu_{C=O}$ (cm^{-1}) substituted Azines versus σ^+

CONCLUSION

When correlations were made for C=N and >N-N stretching frequencies with σ and σ^+ constants only a fair correlation was obtained. Their correlations involving various substituent parameters give positive r values. The correlation of C=N and >N-N stretching frequencies with Hammett substituent constants, σ_I and σ_R parameters collectively explain substituents effect in some cases.

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