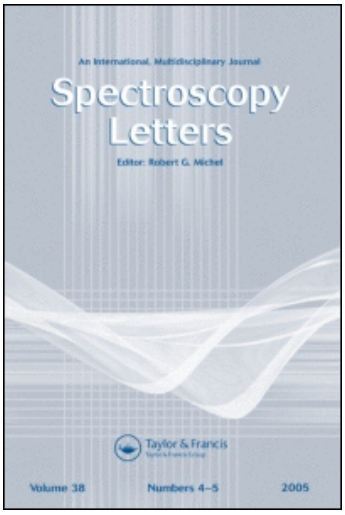

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Tautomerism in Salicylidene Benzylamine

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TAUTOMERISM IN SALICYLIDENE BENZYLAMINE

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ABSTRACT

The UV spectra of substituted salicylidene benzylamine schiff bases were studied in four solvents. It was found that substituents which increase the electronic effect and not the steric compression effect in these compounds increase the percentage of the keto form. The intensity (i.e. % keto) of the keto band which occurs at > 400 nm in the UV spectra increases in polar solvents.

INTRODUCTION

Keto-enol tautomerism in schiff bases is the subject of several studies[1-13]. Schiff bases obtained from the

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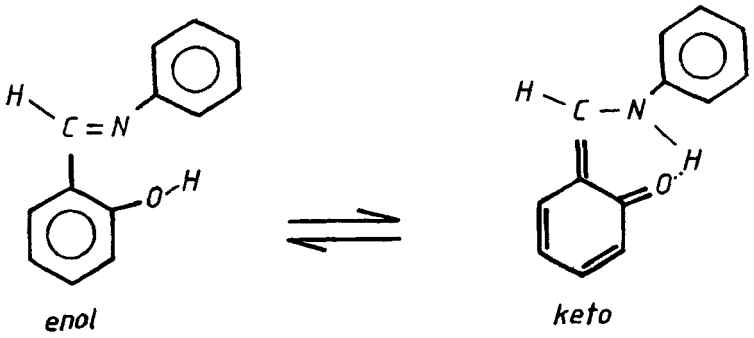
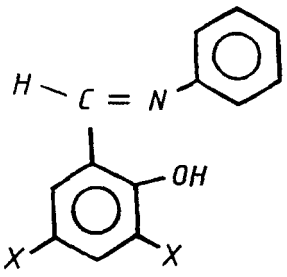


(Scheme 1)



1,X = H; 2,X = t-Butyl; 3,X = I; 4,X = Br

(Scheme 2)

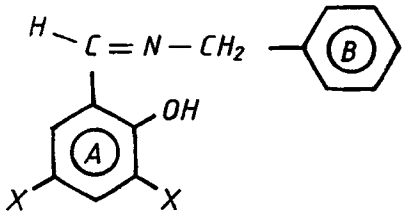
condensation of salicylaldehyde and aniline exist as enol-keto form.

Polar solvents enhance the keto form, thus a new band appears in the UV-visible spectra at > 400 nm which was assigned to the keto form.

Our interest is in obtaining a detailed information on factors affecting this keto-enol equilibrium. In previous work[10-12] we studied systems with different substituents

(Scheme 2)

In this work we present some UV-visible data on the following system in four solvents:



1,X = H; 2,X = t-Butyl; 3,X = Br

(Scheme 3)

The aim of this work is to study the effect of the CH_2 group on the keto-enol tautomerism.

EXPERIMENTAL

Compounds 1-3 in this series were synthesized by the condensation of substituted salicylaldehyde with benzylamine in ethanol and recrystallized from the same solvent. The structure of these compounds were determined from their C,H,N analysis (Table 1) and their ^1H NMR which is characterized by a δOH = 13-14.5 ppm, $\delta CH{=}N$ = 8.3-8.7 ppm, δCH_2 = 4.6-4.9 ppm and δaromatic = 6.9-7.8 ppm. The purity of all compounds was checked by TLC. The melting point of compounds 1-3 was determined using Galenkamp apparatus. The UV-visible spectra were run on a Pye-Unicam SP8-100 spectrophotometer using a quartz cell of 1 cm path length. Optimum concentration of 5×10^{-5} mole was used for all compounds.

Table 1. Elemental analysis and M. Pt. of compounds 1-3.

Compd No	Molecular formula	% C	% H	% N	M.Pt °C
1	$C_{14}H_{13}NO$	79.30 (79.62)	5.90 (6.16)	6.40 (6.64)	37
2	$C_{21}H_{29}NO$	80.60 (81.03)	9.03 (9.32)	4.30 (4.50)	97-98
3	$C_{14}H_{11}Br_2NO$	45.82 (45.55)	3.22 (2.98)	4.96 (3.80)	99-100

( ) Calculated

Table 2. Effect of solvent on the UV spectra of compounds 1-4

Compd	Solvent	λmax (nm)	(ξ m^2 mol^{-1})
1	cyclohexane		320 (760), 257 (1640)
	$CHCl_3$		316 (580), 263 (1780)
	EtOH		392 (88), 322 (660), 303 (1000)
	DMSO		316 (640), 258 (1920)
2	cyclohexane		328 (440), 258 (1412)
	$CHCl_3$		332 (530), 264 (1670)
	EtOH		324ᵃ (692), 254 (3120)
	DMSO		328 (500), 264 (1636)
3	cyclohexane		336 (620), 258 (1510)
	$CHCl_3$	434 (70)	334 (415), 257 (1260)
	EtOH	416 (230)	336 (140), 280 (3050)
	DMSO	424 (425)	334 (205), 262 (8100)
4*	cyclohexane		358 (10485), 271 (13398)
	$CHCl_3$	475ᵃ (971)	355 (11068), 277 (12815)
	EtOH	420ᵃ (1165)	355 (7572), 277 (1160)
	DMSO	446 (2427)	303 (9902), 265 (11844)

* Reference 12.

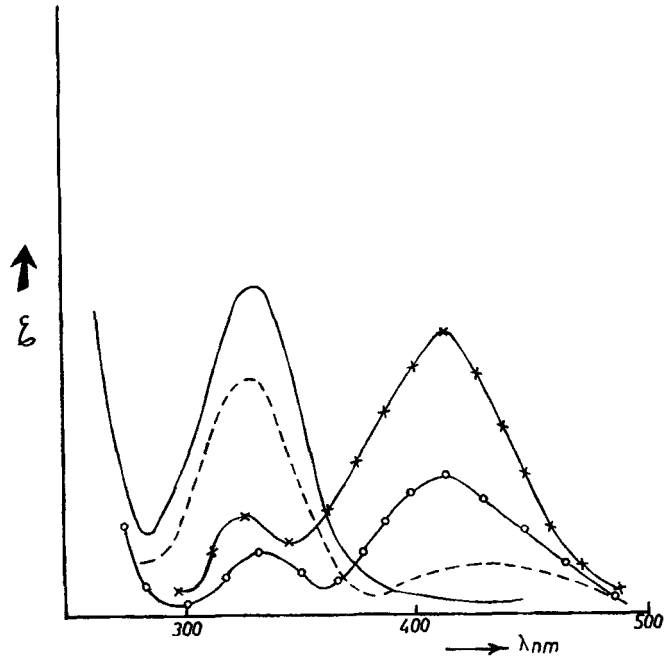


Fig. 1. Solvent effect on compound 3, Cyclohexane ——, Chloroform - - - -, Ethanol o—o, DMSO x—x.

RESULTS AND DISCUSSION

Table 2 gives the UV-visible data for compounds 1-4 in four solvents, whereas Figure 1 shows representative UV spectra of compound 3 in different solvents. From Table 2 and Figure 1 the following remarks may be made:

1. In compounds 1 and 2 no band appears at > 400 nm in ethanol or DMSO indicating that although the compression is very high in compound 2 leading to a stronger

intramolecular hydrogen bonding between O-H and N=CH part but present little possibility of a proton exchange between the oxygen and the nitrogen atom.

2. In compound 3, the proportion of the keto form increases in going from chloroform to ethanol to DMSO and it is the highest in polar solvents. At the same time one observes a blue shift for the keto band in going from chloroform to DMSO to ethanol indicating that the strongest intermolecular hydrogen bonding is formed between the schiff base and ethanol solvent. The same trend was observed with compound 4 (Scheme 2), but in comparing the position and the extinction coefficient of the keto band in compound 3 (Scheme 3) and compound 4 (Scheme 2) one observes that in compound 4 the keto band are red shifted in all solvents indicating a delocalization of the charge throughout the whole molecule, at the same time inhibition of resonance between ring B and the rest of the molecule in compound 3 decreases the percentage of the keto form in all solvents (compare ξ in compounds 3 and 4).
3. One may conclude that in these schiff bases the electronic effect play a major role in enhancing the keto form. Steric and compression factors play no effect in this respect.

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