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Synthesis, Thermochromic Properties and Thermal Behavior of some Schiff Bases. Part I. *p, p′*-Diaminodiphenylmethane-Schiff Bases and Sulphonamide Schiff Base

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Abstract: *p, p′*-Diaminodiphenylmethane-Schiff bases (SB) of general formula (R)-phCH=N-ph-CH_2-ph-N=CHph(R), where R is *p*-NO_2, *m*-NO_2, *p*-OH, *o*-OH, *p*-Cl, -H, *p*-OCH_3, and sulphonamide Schiff bases (SB) of general formula (R)-phCH=N-ph-SO_2NH_2, where R is *p*-NO_2, *m*-NO_2, *p*-OH, *o*-OH, *p*-Cl, -H, *p*-OCH_3, were synthesized and their structure have been characterized by the melting pointing, ^{1}HNMR, MS, and elemental analysis. They are thermolabile and undergo thermo-chromism and thermal decomposition after melting. The TG. and DSC measurement were recorded in dynamic air and interpreted.

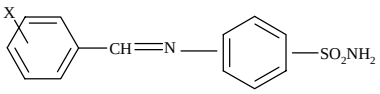
Keywords: *p, p′*-Diaminodiphenylmethane, Schiff bases, thermochromic, sulphonamide.

Crystalline salicylideneaniline and its derivatives exhibit thermochromic phenomena, *i.e.*, they show a reversible colour change, as a result of a variation in temperature[1-3]. The presence of the *ortho*-OH group is considered to be an essential condition for the thermochromic effects[4]. One study[5] has indicated that the presence of an ortho-hydroxyl group is not a structural requirement for the thermochromism of Schiff bases. However, in this literature only differential thermal analysis (DTA) was reported.

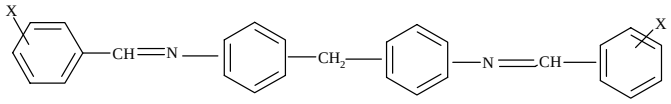
The synthesis of the *p,p′*-diaminodiphenylmethane Schiff bases and sulphonamide Schiff bases is reported in this article. Among them ten are new compounds and their structures have been characterized by melt point, ^{1}HNMR, MS and elemental analysis.

Eight of these Schiff bases are reversible thermochromic and the color change of these compounds are quite obvious. The thermochromic behaviour of the Schiff base is recorded by differential scanning calorimetry (DSC) and TG. The kinetic parameter, activation energy of the peak of thermocolor points has been calculated.

The Schiff bases included in the present investigation have the general formula as follows:



X=*p*-NO_2 (I_1), *p*-OH (I_2), *p*-OCH_3 (I_3), *o*-OH (I_4), *p*-Cl (I_5), -H (I_6)



X=*p*-NO_2 (II_1), *p*-OH (II_2), *p*-OCH_3 (II_3), *o*-OH (II_4), *p*-Cl (II_5), -H (II_6), *m*-NO_2 (II_7)

Experimental

The Schiff bases were prepared from *p, p'*-diaminodiphenylmethane and sulphonamide by reaction with benzaldehyde and its derivatives in absolute ethanol, according to a procedure adapted from Diehl and Hach's method[6]. The compounds were purified by recrystallezation with acetone.

Carbon, hydrogen and nitrogen contents of two series Schiff base were indicated by standard microanalytical procedures. Melting points were determined on a X_4-Temp apparatus and the themometer is uncorrected. ^{1}HNMR spectra were recorded on a Bruker. Cxp-200 spectrometer using $CDCl_3$ and DMSO as solvent and tetramethylsilane as internal reference

DS (TG) analysis of eight reversible thermochromic Schiff bases were carried out at a heating rate of 10^{o}C min^{-1} in air using a Perkin-Elmer DSC7 thermal analyzer.

Results and discussion

A summary of the thermochromic properties of the polycrystalline powders see **Table 1**. The DSC data of the reversible thermochromic Schiff bases were recorded and summarized in **Table 2.**

Table 1 Thermochromic Behavior of the SB(I) and SB(II) under investigation.

SB	Thermochromic	Transition T/°C	Color change*
I_1	Irreversible		Greenish yellow to Deep yellow
I_2	Irreversible		Pale yellow to Yellow
I_3	Reversible	86	White to Pale green
I_4	Reversible	82	Yellow to Red
I_5	Reversible	106	White to Green
I_6	Reversible	120	White to Pale green
II_1	Irreversible		Yellow to Greenish yellow
II_2	Irreversible		Yellow to Deep yellow
II_3	Reversible	55	Pale yellow to Greenish yellow
II_4	Reversible	100	Yelllow to Red
II_5	Reversible	150	White to Pale yellow
II_6	Reversible	100	White to Pale yellow

The DSC data shown in **Table 2** indicate that the compounds SB (I) and SB (II) are pure. The ΔH (ΔS) values of these endomeric peaks exhibit following relationship: $I_4 > I_3 > I_5$ and $II_4 > II_3 > II_5$. This can be explained in terms of the structural stability effected by the substituting group: SB(I_4) and SB(II_4) both exists *o*-OH group, which can form hydrogen bond of inner molecular, both SB (I_3) and SB (II_3) exists *p*-OCH_3 group and can form strong p-π conjugation between the oxygen atom and the benzene nucleus.

both SB (I_5) and SB (II_5) exist *p*-Cl substitute which has accepting effect as well as donating electron effect for benzene nucleus. It can be concluded that the ΔH (ΔS) values of the melting point peaks are effected greatly by substitute of the benzene nucleus.

Due to the decomposition point peaks of SB (I) were followed by broad exothermic peaks in the range 283°C~414°C. The ΔH values of these exothermic peaks of SB (I) are in the range -13.67 kJ/mol ~ -49.41 kJ/mol.. Also due to the decomposition point peaks of SB (II) were followed by broad exothermic peaks in the range 270°C~353°C. The ΔH values of these exothermic peaks of SB (II) are in the range -39.90 ~ -56.43 kJ/mol. The ΔH values of SB (II) are more larger than SB (I) which probably result from the molecular link of SB (II) is longer and more molecular bonds needed to break than that of SB (I).

For the compounds SB(II), the ΔS is increasing depend on the temperature.

It is interesting to observe that the color changing peaks of SB (II_3) and SB (II_5) are below the melting point. But none of SB (I) shows color changing peaks.

The temperature ranges of the color changing peaks appropriately conform to the transition temperature ranges in which the SB (II_3) and SB (II_5) show thermochromism respectively. It can be concluded that the SB (II_3) and SB (II_5) under investigation exist the balance between the before color change phase and the after color change phase.

Table 2 DSC data.

SBs	T/°C	Peak T./°C	ΔH_1 KJ/mol	ΔH_2 KJ/mol	ΔS_3 KJ/(mol.J) 10^3
I 3	180-205	200.3	+12.28	+12.29	25.9
	272-318	314.6	-13.67	-13.67	23.3
I 4	205-223	215	+16.90	+16.90	34.6
	283-353	312	-34.60	-34.60	58.9
I 5	184-207	200.5	+9.67	+9.65	20.4
	270-322	298.8	-21.91	-21.87	38.2
I 6	171-199	192.6	+28.89	+28.00	62.0
	278-315	305	-49,41	-49.41	20.4
II3	49-59.6	52	-0.96	-0.97	2.9
	154-170	164.3	+12.86	+12.86	29.4
	338-396	373.1	-54.19	-54.00	83.9
II4	205-217	213	+16.86	+16.86	34.7
	283-389	353.6	-39.91	-39.90	63.7
II5	153-164	158.5	+1.91	+1.91	4.4
	176-187	184	+9.68	+9.96	21.1
	295-400	376.6	-56.56	-56.43	86.9
II6	121-134	130.3	+8.66	+8.66	21.5
	300-414	384.2	-50.08	-50.08	76.2

1: (-) exo, (+)endo;
2: ΔS=ΔH/T peak temp (K)

Acknowledgment

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