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Thermal behaviour and electrical properties of some biologically active sulphonamide Schiff bases

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Abstract

The sulphonamide Schiff bases are thermolabile and undergo thermochromism and thermal decomposition after melting. The electric conduction properties of the Schiff bases were studied. In addition, the current–voltage dependence of the sulphonamide Schiff bases was investigated. This showed that the Schiff bases under investigation have ohmic conduction which is temperature independent.

INTRODUCTION

Schiff bases (SB) derived from sulphonamide have wide application to biological [1], clinical [2] and pharmacological systems [3,4]. The complexes of selenium(IV) and tellurium(IV) with sulphonamide Schiff bases have been studied using bacteriostatic, anti-inflammatory and hupogly cemic tests [5]. The use of thermal methods of analysis as a technique for studying the bonding and structure of coordination compounds has increased greatly in the last few years [6].

The present work was undertaken to ascertain the thermal stability and to obtain information about the electrical conductivity of these compounds. In addition the current–voltage ($I-V$) characteristics for some SBs were studied at different temperatures.

EXPERIMENTAL

The sulphonamide was obtained from the Aldrich chemical company. All other materials used in this work were of pure grade.

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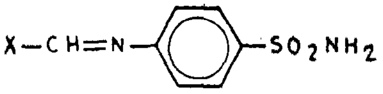
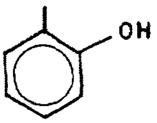
The ligands were prepared by the method of Diehl and Hach [7]. The sulphonamide Schiff bases included in the present investigation have the general formulae



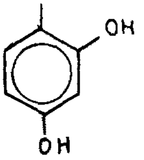
(I)

(II)



(III)

(IV)



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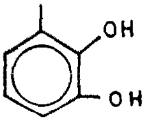

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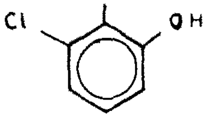

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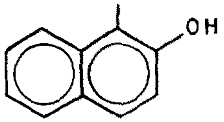

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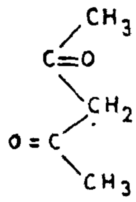


(IX)

Differential thermal analysis (DTA) of the samples (10–14 mg) was carried out at a heating rate of 10 °C min^{-1} in air using a Shimadzu XD-30 thermal analyser. X-ray powder diffraction patterns of the Cu$K\alpha$ line were obtained on a Shimadzu XD-3 diffractometer. The electrical conductivity (σ) and the current–voltage dependence were measured using a super Megohmmeter (Model 170), as described elsewhere [8].

RESULTS AND DISCUSSION

The thermochromic properties of the polycrystalline powders are shown in Table 1. The DTA diagrams of the Schiff bases were recorded and their data are summarised in Table 1 and Fig. 1). The results can be classified into

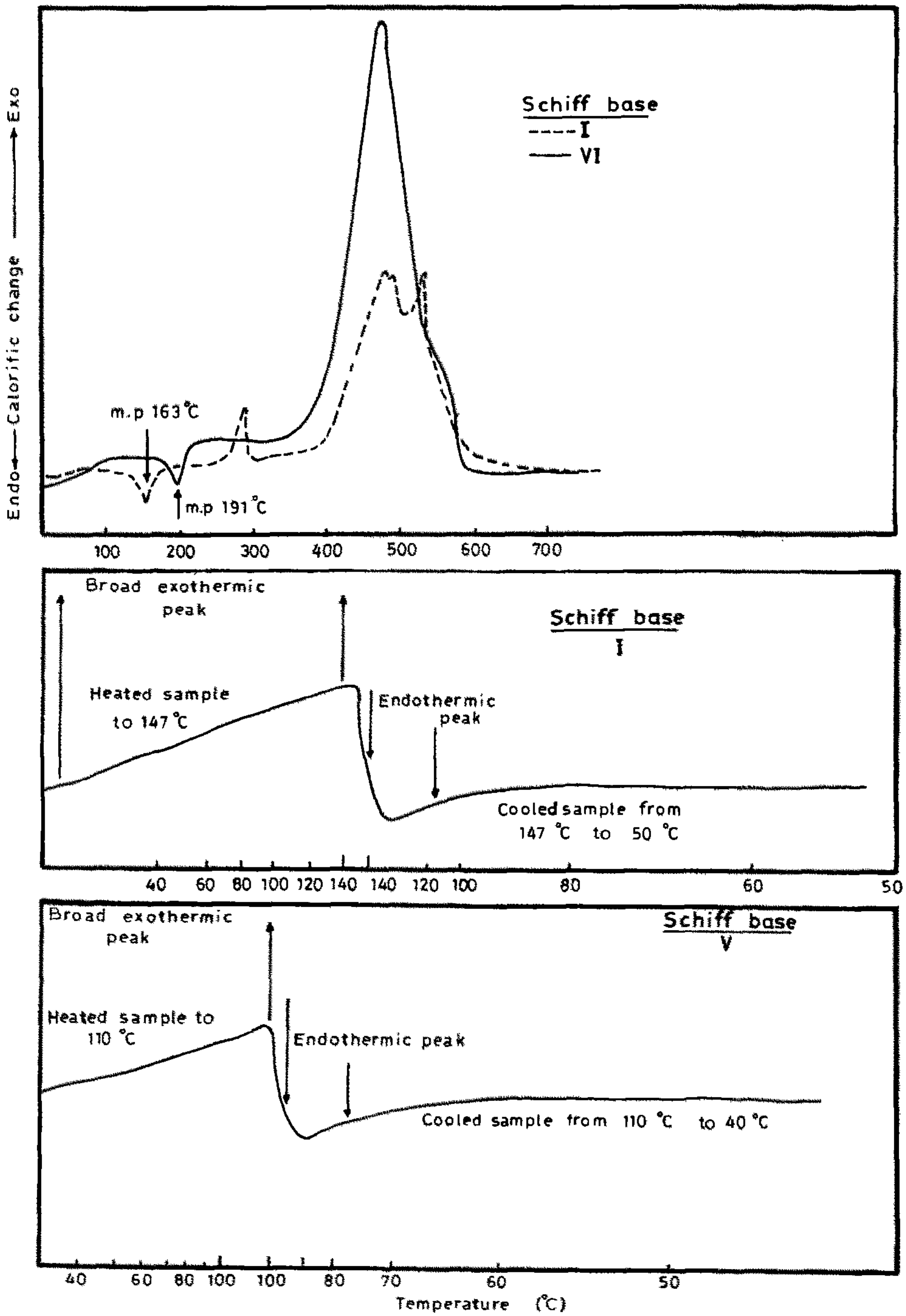


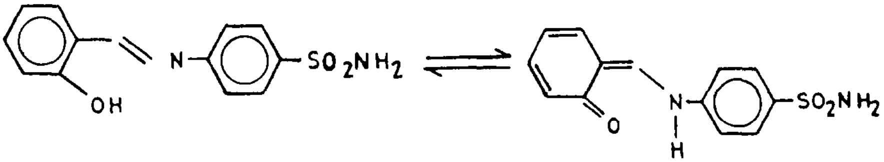
Fig. 1. DTA curve of Schiff bases I, V and VI.

TABLE 1

Thermal behaviour of the Schiff bases under investigation

SB	Property	Colour change
I	Thermochromic	
II	Thermochromic	Lemon ⇌ yellow
III	Thermochromic	Yellow ⇌ red
IV	Thermochromic	
V	Thermochromic	(Orange-red ⇌ dark brown)
VI	Thermochromic	
VII	Thermochromic	Yellow ⇌ orange
VIII	Thermochromic	Buff ⇌ light brown
IX	Photochromic	Yellow ⇌ light orange

two sets: first, those heated below the melting point and then cooled; and second, those heated until melting. Examination of the results shows that thermochromism is displayed as a colour change: yellow ⇌ orange and orange ⇌ red. In the solid state via a thermal process, SB (III) and SB (VIII) show the colour changes yellow ⇌ red and buff ⇌ light brown, respectively. This can be explained in terms of thermal enol ⇌ keto tautomerism [9]



On heating, all sulphonamide Schiff bases gave broad exothermic peaks but when cooled endothermic peaks were observed and the original colours readily reappeared.

It can be concluded that all (SB's) under investigation undergo reversible colour changes under the influence of temperature. Also, the thermal stability in the solid state (prior to melting) was established [10].

The endothermic peaks for SB (I) and SB (VI) indicate the melting of the compounds. These were followed by broad exothermic peaks in the range 267–457 °C that are due to decomposition. Thermochromism was not observed for SB (IX): however, a colour change from yellow to light orange was observed after prolonged standing. Therefore, X-ray diffraction of the relevant SB was measured just after preparation and after four months, see Fig. 2 which illustrates that the X-ray patterns are different. This could be attributed to structural changes caused by photo-induced molecular rearrangements which probably result from changed molecular interaction and packing in the solid lattice [11].

ELECTRICAL CONDUCTIVITY

The electrical conductivity (σ) of the various Schiff bases was measured. Figure 3 shows the plots of log σ versus the reciprocal absolute temperature

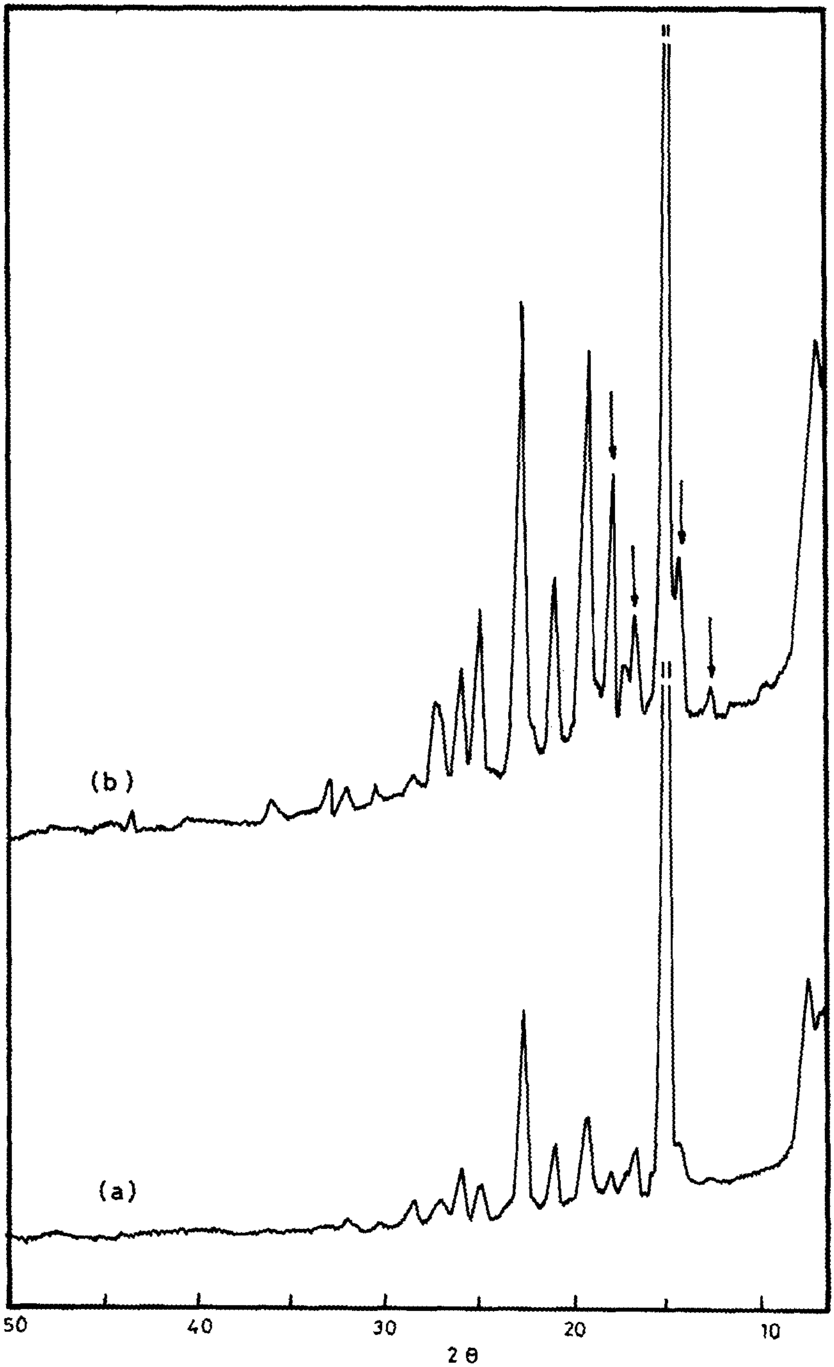


Fig. 2. X-ray powder diffraction of Schiff base IX.

$(1/T)$, in accordance with the equation

$$\sigma = \sigma_0 \exp(-\Delta E/KT)$$

where σ is the electrical conductivity at a given temperature T, σ_0 is the

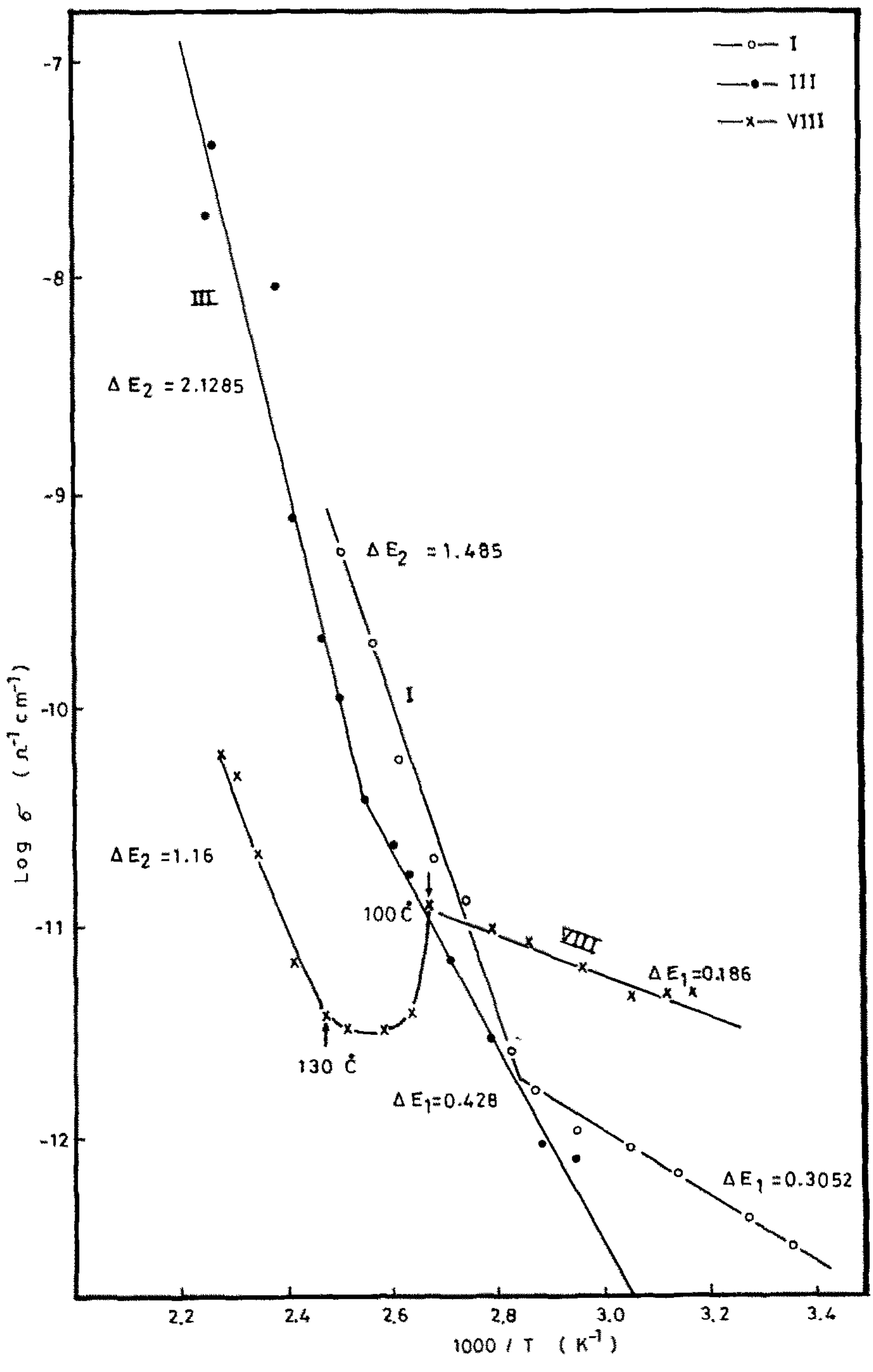


Fig. 3. Temperature dependence of the electrical conductivity of Schiff bases **I**, **III** and **VIII**.

TABLE 2

The electrical conductivity σ (Ω^{-1} cm^{-1}) at 40 °C and the activation energies, ΔE_1 and ΔE_2, for the investigated SBs

SB	M.p. (°C)	σ	Transition temp. (°C)	ΔE_1 (eV)	ΔE_2 (eV)
I	166	5.01×10^{-13}	79	0.305	1.485
II	205	15×10^{-13}	45	0.292	1.128
III	184	3.16×10^{-13}	120	0.928	2.1285
IV	189	5.62×10^{-13}	105	0.083	0.841
V	120	2.51×10^{-10}	117	0.752	1.399
VI	190	11.2×10^{-13}	74	0.223	0.871
VIII	260	21.1×10^{-13}	100 and 130	0.186	1.16
IX	180	56.2×10^{-13}	97	0.578	1.782

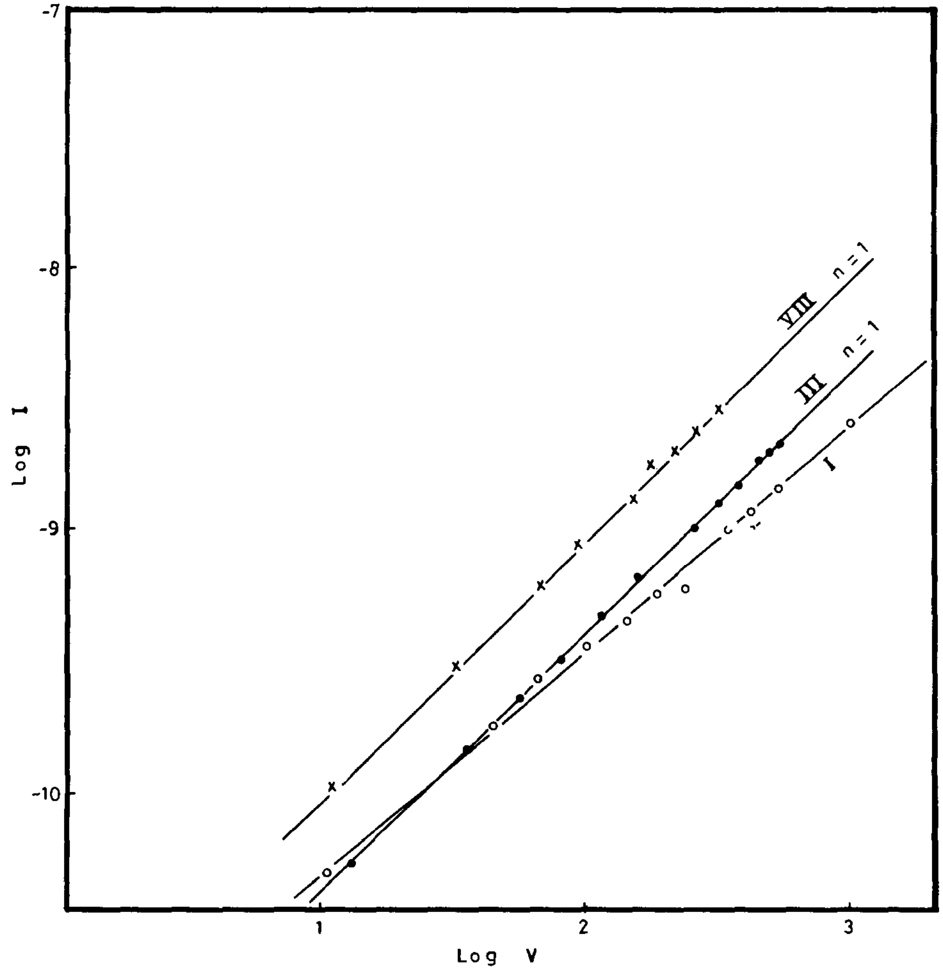
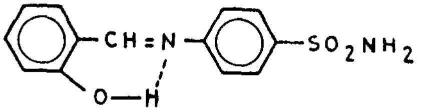


Fig. 4. Log I vs. log V for Schiff bases **I**, **III** and **VIII** and their values of n at different applied voltages.

pre-exponential factor, ΔE is the activation energy for conduction and K is the Boltzmann constant. From this linear relationship, the activation energy, ΔE can be calculated. The ΔE values can be interpreted by a band model containing a partially occupied set of trap states near the centre of the energy gap between valence (¶) and conduction (¶*) bands.

It can be shown that the conductivity of all samples under investigation increases with increasing temperature. Hence, they exhibit semiconducting properties. In addition, most of the SBs have two modes of conduction and, therefore, have two activation energy values, ΔE_1, and ΔE_2. SB (VIII) has two modes of conduction and two transition temperatures at 100 and 130 ° C. The discontinuity in the semiconducting region can be ascribed to a molecular rearrangement [12] and the shallow behaviour in the temperature range 100–130 ° C can be attributed to the thermal enol $\rightleftharpoons$ keto tautomerism [9]. Therefore, it would be reasonable to assume that the first step in the conduction process is a delocalisation of ¶-electrons. The second step involves the excitation of an electron from the highest filled ¶-molecular orbitals to the lowest unfilled ones [13]. The decrease in the conductivity of SB (II) and SB (VIII) at higher temperatures may be attributed to dissociation in the sample network.

The deduced ΔE and σ values at 40 ° C are collected in Table 2. These data show that the activation energies are highly dependent on the molecular structures of the Schiff bases. The conductivity values do not show large variations. The higher σ and lower ΔE values of SB (II) can be ascribed to the intermolecular hydrogen bond formation between the hydroxyl group and amino group [14]. A reverse effect was observed in the case of the presence of the hydroxyl group in the ortho position in SB (III). This can be attributed to intramolecular hydrogen bond formation which can localise charge carriers and inhibit their mobility between different molecules.



The conductivity of the *p*-chlorosubstituted (IV) was not enhanced, and the activation energies decreased in comparison with SB (I). The substituent may enhance intramolecular charge migration [14].

The di-substituted hydroxyl Schiff bases have in general higher σ and lower ΔE values than unsubstituted or mono-substituted ones. Hydroxyl substitution in the meta position (VI) decreases the probability of hydrogen bond formation between *o*-OH and the nitrogen of the azomethine. The keto–enol tautomerism occurring at higher temperatures in SB (V) decreases this hydrogen bond formation.

The activation energy of SB (VIII) is lower than those of SB (I) and (III). This can be attributed to the increased electron density due to the higher

TABLE 3

The values of n of the proportionality $I\alpha V^n$ at different applied voltages and temperatures, with the correlation coefficients of the plots, R

SB	Applied voltage (V)	Temp. (°C)	n	R
I	10–490	29	0.95	0.991
	10–250	69	0.961	0.998
	10–190	132	0.918	0.998
II	10–430	68	1.098	0.995
III	10–260	28	1.11	0.998
	10–410	71	0.925	0.999
	10–490	122	0.994	0.999
IV	10–470	70	0.89	0.997
	10–490	131	0.949	0.999
V	10–440	47	1.058	0.999
	10–490	88	1.11	0.993
	10–490	106	0.979	0.995
VIII	10–270	27	1.037	0.999
	10–340	72	1.034	0.997
IX	10–490	46	1.107	0.996
	10–490	91	1.149	0.998
	10–440	108	1.11	0.992

donor character of the naphthalene ring. A contrasting behaviour was observed in the case of SB (**IX**) in which the phenyl ring was substituted with acetyl acetone.

The currents (I) were measured at different applied voltages (V) and at different temperatures to establish the I–V characteristics. It can be shown from the plots of log I versus log V (Fig. 4 and Table 3) that a proportionality $I\alpha V^n$ is obtained with $n \approx 1$. In addition, this behaviour is temperature independent. Therefore, it is concluded that all the samples obey Ohm's law.

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