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THE ELECTRICAL PROPERTIES OF SOME 2-AMINOPYRIMIDINE AND 2-AMINOPYRAZINE SCHIFF BASES

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ABSTRACT

The electrical properties of some Schiff bases of 2-aminopyrimidine and 2-aminopyrazine with benzaldehyde derivatives have been investigated. Such measurements have rarely been done on these compounds. The positive temperature coefficient of electrical conductivity ($d\sigma/dT$) found for all the samples investigated is evidence for the semiconducting character within the range of temperature studied. For the compounds studied, a correlation between the electrical properties and their chemical structure is established. The mechanism of the conduction process in these samples is also studied.

INTRODUCTION

Numerous experimental and theoretical studies have been performed with the objective of establishing a correlation between the semiconducting properties of organic compounds and their chemical structure [1]. Schiff bases were the subject of many such studies. Schiff bases are used as chemical intermediates, perfume bases in dyes, rubber accelerators and in liquid crystals for electronics. Gooden [2] studied the electrical conductivity of Ag-coated polycrystalline pellets of anils derived from salicylaldehyde and *meta-* or *para*substituted anilines. Aromatic Schiff bases derived from the *p*-substituted benzaldehydes, 9-anthraldehyde and 1, 2-naphthaldehyde, have also been studied [3]. Avramovici [4] measured the electrical conductivity of some salicylidenanils.

Recently Abou Sekkina and Issa [5] gave a detailed account of the semiconductivity, electrical conductivity and optical properties of different substituted Schiff bases with a view to their possible application in solar cells. The authors observed that the electrical conductivity increased and both the activation energy and energy gap decreased with increased electron density and polarization of the donor molecule as a function of substitution

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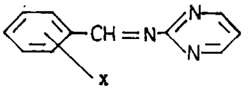
mode and magnitude. This in turn facilitates the ionization mechanism and electron flow allowing electronic- and/or ionic-conduction mechanisms to take place.

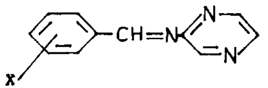
The aim of the present work is to study the current–voltage characteristics, the electrical conductivities and the dielectric constants of Schiff bases derived from 2-aminopyrimidine and 2-aminopyrazine with some benzaldehyde derivatives in order to search for a compound of semiconducting character, which may be used in a solar cell with high efficiency. Such measurements have rarely been done on samples of this type.

EXPERIMENTAL

All chemicals used were of the purest grade provided by BDH (England) and Schuchardt (Munich). The Schiff bases under investigation were prepared by fusion [6] of equimolecular amounts of 2-aminopyrimidine (**I**) (0.1 mol) or 2-aminopyrazine (**II**) (0.1 mol) with the corresponding aldehyde (0.1 mol) on a hot plate with constant stirring. Some solids were separated while heating and others were separated after cooling. The crude Schiff base was recrystallized several times from ethyl alcohol until a constant melting point was reached. The Schiff bases prepared were



[I]



[II]

where X is (**a**) H, (**b**) *p*–OCH_3, (**c**) *p*–Cl, (**d**) *p*–NO_2, (**e**) *p*–$N(CH_3)_2$, and (**f**) *o*–OH.

For electrical measurements the samples (Schiff bases) were pressed into pellets at a pressure of about 600 kg cm^{-2}, which was chosen because at this pressure the electrical conductivity was independent of load [5]. Two thin copper wires of diameter 0.25 mm were attached to the two major surfaces of the pellet which were carefully painted with conducting silver paste (Degussa, F.R.G.). A regulated electrical oven was used to control the ambient temperature in the range 20–120 °C. The measurements were carried out at a rate of about 1 °C min^{-1}. Samples were subjected to moderate heating for 1 h in order to minimize surface conductivity before measurements.

The conduction current was measured using a 610 C electrometer (Keithley instruments). The minimum current which can be measured by this instrument is 10^{-4} A with an accuracy of ± 2–4%. The dielectric constant was measured using a precision capacitance bridge (Tesla, BM 400 G) working at 800 Hz and with a least count of 10^{-4} PF.

RESULTS AND DISCUSSION

The following discussion is concerned with some Schiff bases of 2-aminopyrimidine or 2-aminopyrazine with benzaldehyde derivatives (Table 1).

Typical characteristic curves ($I-V$) are shown in Fig. 1. It is seen that a straight line relation is obtained, which indicates that the compounds under investigation have ohmic character (i.e., obey Ohm's law).

Figure 2 shows the temperature dependence of the electrical conductivity of the Schiff bases. It is obvious from the curves that electrical conductivity increased with a continuous rise in the temperature. This positive temperature coefficient of electrical conductivity ($\mathrm{d}\sigma/\mathrm{d}T$) for all the bases investigated is evidence for semiconducting character within the range of temperature investigated. It is clear that the increase of temperature obeys the usual exponential law:

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

where σ is the electrical conductivity at a given absolute temperature T, σ_0 is the initial conductivity (the pre-exponential factor), ΔE is the activation energy of conduction, and K is the Boltzmann constant. The activation energy ΔE was calculated from this exponential relation.

Most of the temperature-dependence/electrical-conductivity curves obtained are characterized by two activation-energy values. This means that the mode of conduction changed during the conductivity measurements. It is thus assumed that the first step in the conduction process is essentially due to electronic conduction through the delocalization of the π electrons. While for the second step, which occurs at high temperatures, the conduction is due to the excitation of an electron from the highest filled π molecular

TABLE 1

Electrical conductivities, σ, at room temperature, and activation energy, ΔE

Compound	Melting point (°C)	σ (Ω^{-1} cm^{-1})	ΔE (eV)	
			Lower temp. range	Higher temp. range
Ia	188	1.4×10^{-13}	0.26	0.46
Ib	166	1.3×10^{-11}	0.65	–
Ic	155	1.8×10^{-11}	0.69	–
Id	88	4.0×10^{-12}	1.05	–
Ie	63	7.4×10^{-11}	1.38	2.12
IIf	108	1.5×10^{-12}	0.89	1.25
IIe	60	6.6×10^{-10}	1.29	2.11

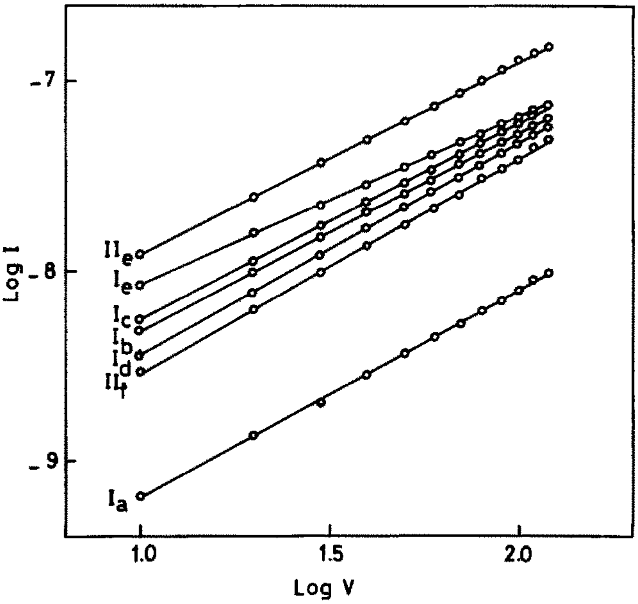


Fig. 1. The current–voltage characteristics ($I-V$) of some 2-aminopyrimidine (**I**) and 2-aminopyrazine (**II**) Schiff bases.

orbital to the lowest unfilled π molecular orbital. Thus, the electron is assumed to tunnel to an equivalent empty level of a neighbouring molecule in the anodic direction, whereas the positive hole moves to a molecule in the cathodic direction. The decrease in the electrical conductivity of compounds **Ia**, **Ib** and **Ic** at higher temperatures may be due to the damage in the network of the samples and the decrease in the number of free radicals due to recombination.

The electrical conductivity, therefore, depends largely on the chemical structure of the compounds investigated (Table 1); this may be due to the increased electron migration and the resulting polarization of the molecule under the influence of substitution. In fact, substituents may facilitate the ionization mechanism and electron flow.

The relatively low electrical conductivity observed for **Ia**, with respect to **Ie**, can be explained on the basis that the heterocyclic ring is the origin of intramolecular charge migration, i.e., the charge migrates from the anil heterocyclic ring to the benzal ring, which is in accordance with previous studies. Conversely, for **Ie**, which has $N(CH_3)_2$ groups on the benzal ring, an intramolecular charge migration from the benzal ring to the heterocyclic ring is expected. Such an effect will counter the charge migration from the heterocyclic ring to the benzal ring. The net result of these two counter effects will increase the charge delocalization and, consequently, the electri-

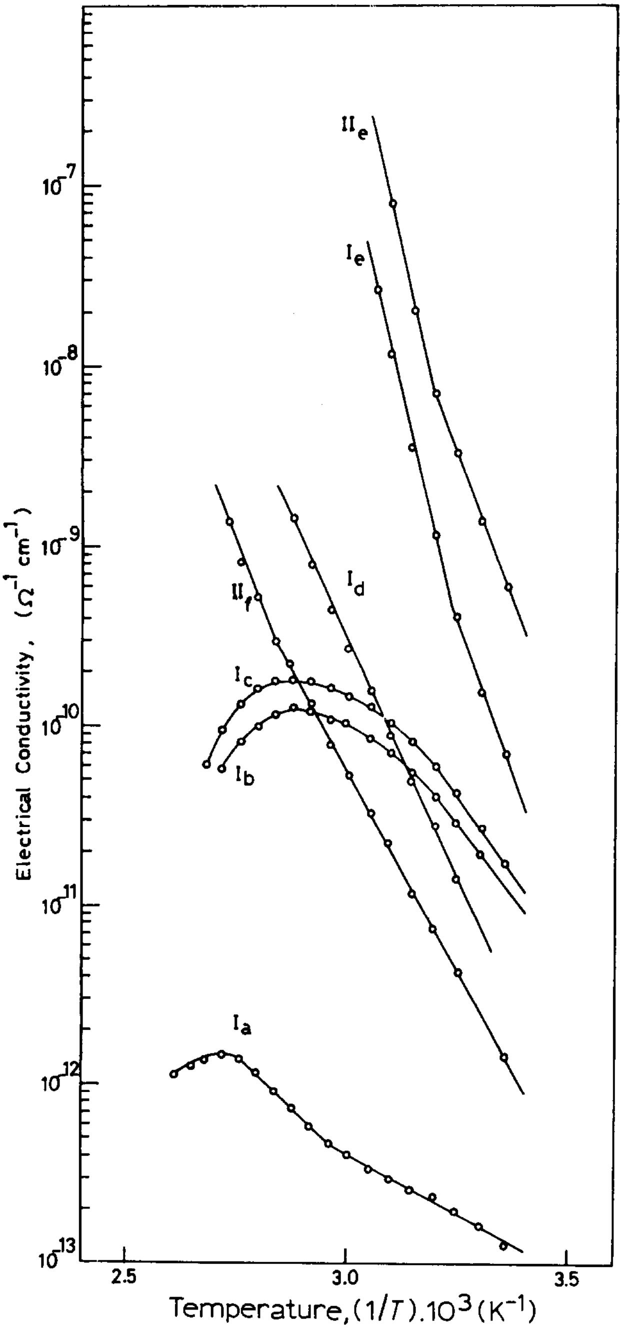
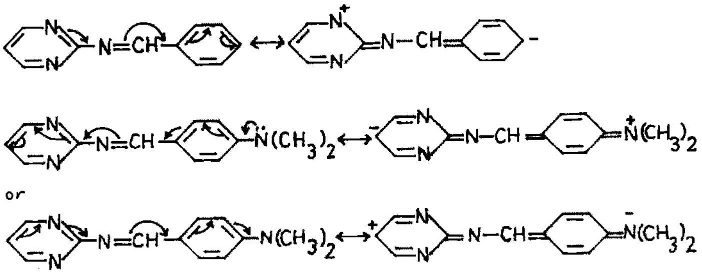


Fig. 2. The variation of electrical conductivity as a function of reciprocal absolute temperature for some solid Schiff bases.

cal conductivity increases. Thus:



It can be deduced from the data in Table 1 that the presence of electron-donating groups on the benzal ring will counter the intramolecular

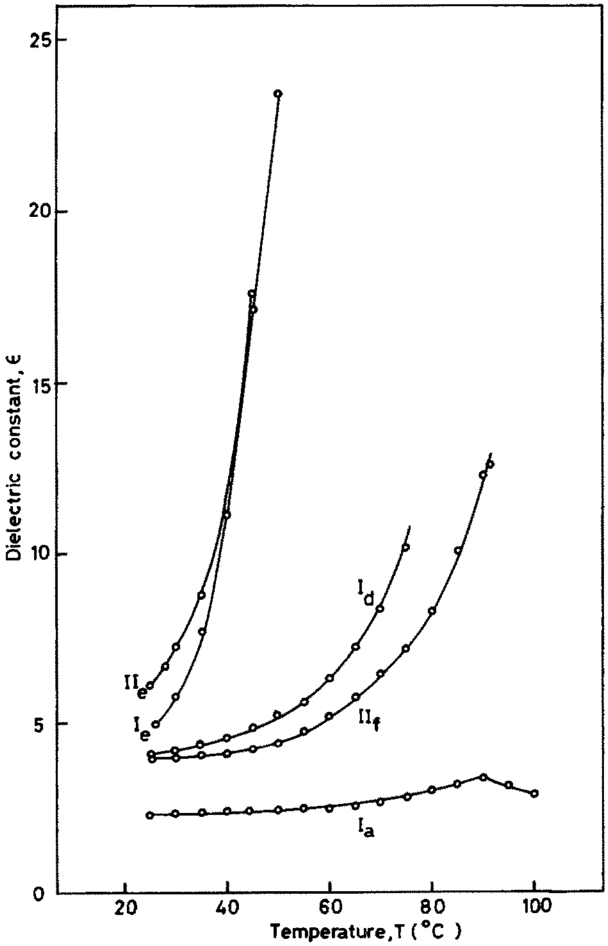
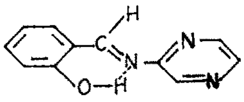


Fig. 3. The dielectric constant as a function of temperature for some solid Schiff bases.

charge migration from the heterocyclic ring to the benzal ring, thus accounting for the observed increase of electrical conductivity. On the other hand, the presence of electron-withdrawing groups (e.g., NO_2, Cl) on the benzal ring will assist the intramolecular charge migration; this probably increases the polarization of the donor molecule. The observed result is an increase of electrical conductivity.

The low activation energy of compound **IIf** (*o*-hydroxy), may be attributed to the existence of the intramolecular hydrogen bond which causes a rise in the ground-state energy, thus facilitating the electronic migration within the molecule.



In the case of the Schiff base **IIe**, the above mentioned discussions for **Ie** holds true.

The dielectric properties of such compounds depend on the chemical structure, the types of impurities, anisotropy and homogenity. Figure 3 shows the variation of the dielectric constant in the temperature range 25–100°C for the different samples **Ie**, **Ia**, **Id**, **IIe** and **IIf** at constant frequency (800 Hz). The dielectric constant, ϵ, increased with temperature, which confirms the previous measurements on electrical conductivities. The samples which contain *p*-*N*-dimethyl showed a sharp increase in dielectric constant with temperature (25–50°C) compared to the other samples. Figure 3 confirms the correlation between the dielectric constant, ϵ, and the chemical structure of such compounds.

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