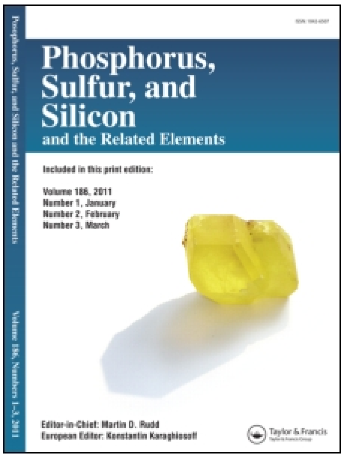

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TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY IN SCHIFF BASE OF 2-NH_2-3-CN-4,5,6,7-T.H. BENZO[B]THIOPHENE AND ITS DIPHENYLPHOSPHINE DERIVATIVE

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Relation of the electrical conductivity as a function of temperature and the molecular structure data including infrared and ultraviolet spectra of p-methoxybenzylidene-2-amino-3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophene and p-methoxybenzylidene-diphenylphosphine-2-amino-3-cyano- 4,5,6,7-tetrahydrobenzo[b]thiophene compounds has been investigated. The results of the electrical conductivity, thermal activation energies obtained from electrical conductivity measurements as well as the energy gaps calculated from ultraviolet (UV) spectra in the solid state are consistent with those of semiconductor materials. The delocalized-π-electrons in addition to the lone pairs of electrons on nitrogen atoms of azomethine groups of the two compounds were considered the main sources participating in the conduction processes

Keywords: Thiophene; Temperature Dependence; Conductivity; Schiff Base

INTRODUCTION

In several earlier papers [1] the study of relationship between electrical conductivity and chemical structure of inorganic and organic compounds has been established. The present work is part of a continuing study in our laboratory, aiming to investigate the electrical conductivity of Schiff base of 2-NH_2-3-CN-4,5,6,7 T.H.benzo[b]thiophene (SB) and its Diphenyl-

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phosphine derivative (OPSB) Compounds on the bases of their spectroscopic structural data [2]. Attempts to interpret the electrical properties of a number of Schiff bases which involve the azomethine group (>C=N-) and the similar compounds like Oximes (>C=N-OH), the hydrazones (>C=N-NH_2), and the Azines $(>C=N-)_2$ and relating these properties to the chemical structure have been carried out [3–5]. It is well be established that the electron system of the highly conjugated compounds is easily delocalized along the molecular skeleton that facilitate their semiconductivity properties. Thus the Schiff base and its diphenylphosphinyl derivative of the present paper have been chosen to study the electrical conductivity (σ), infrared and ultraviolet absorption spectra in relation to their chemical constitution to reveal the effect of diphenylphosphinyl group on the semiconducting properties of Schiff base

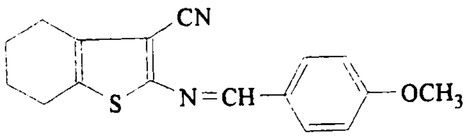
EXPERIMENTAL

the chemicals used in this work were of either Merch or Aldrich quality. Schiff base of 2-NH_2-3-CN-4,5,6,7-T.H.Benzo[b]thiophene (SB) Scheme (1) was prepared and purified as follows: A mixture of equimolecular amounts of p-anisaldehyde (3.1gm, 0.1M) and 2-amino-3-cyano-4,5,6,7tetrahydrobenzo[b]-thiophene (4.45 gm, 0.1M) were heated in a little ethanol till boiling for two hours. The residue was cooled and the product was recrystallized from ethanol giving a yellow crystalline compound. On the other hand, diphenylphosphine derivative of Schiff base Scheme (II) was prepared as follow: A solution of diphenyl chlorophosphine (2.2 gm, 0.01 M) was added to a well stirred solution of equimolecular amount of Schiff base (2.6 gm, 0.01 M) in the presence of triethylamine as a base in 100 ml of dry benzene. After complete addition, the reaction mixture was refluxed for three hours. The solid formed (triethylaminehydrochloride) was filtered off and the filtrate was evaporated in vacuum giving p-methoxybenzylidene-diphenylphosphine-2amino-3cyano-4,5,6,7-tetrahydrobenzo[b]-thiophene which was recrystallized from DMF as a crystalline compound. The prepared compounds (SB) and (OPSB) were checked by thin layer chromatography (TLC) and identified by elemental analysis Table (I). Infrared spectral analysis was carried out at 28±0.1°C as KBr-mixed discs using a Shimadzu IR 440. Ultraviolet absorption spectra were recorded using a Perkin-Elmer lambda 3B. The

^{1}H-NMR spectra of Schiff base and OPSB were recorded by a Varian-EM-360L 90 MHz spectrophotometer. The NMR spectra of (SB) indicate the presence of azomethine proton at δ 8.3, methoxy protons at δ 3.9 and aromatic protons at δ 6.8–8.0 ppm. On the other hand the NMR spectra of OPSB indicate disappearance of azomethine proton of the SB due to the replacement of the hydrogen atom by the diphenylphosphinyl group. The methoxy protons of OPSB were appeared at δ 3.7 ppm and the aromatic protons signals at δ 6.7- 8.2 ppm. The electrical conductivity (dc) data were collected at different temperatures, from room temperature up to near the melting point of each sample in the ohmic region by using the potential probe method [6]. The samples were in the form of pellets pressed at 4 tons/cm^2, diameter~10 mm and thickness 1–2 mm, coated with silver paint (BDH) and checked several times for good contact.

TABLE I Chemical Analysis and melting points of the Schiff base (SB) and the organo-phosphorus Schiff base (OPSB)

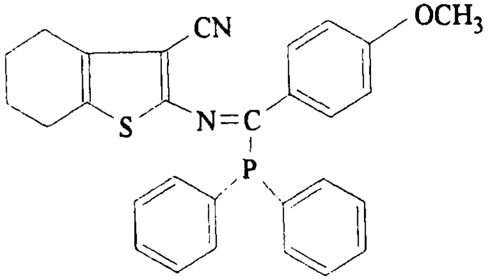
Com-pound	*Colour*	*Solvent used for Cry.*	*m.p. °C*	*Chemical Analysis*							
				% Calculated				*% Found*			
				C	*H*	*N*	*P*	*C*	*H*	*N*	*P*
SB	Deep yellow	Ethanol	130	77.2	6.1	10.6	–	77.4	5.8	10.3	–
OPSB	Yellow	DMF	210	77.6	5.6	6.2	6.9	77.3	5.2	6.4	7.2



SCHEME 1 Molecular Configuration of (SB)

RESULTS AND DISCUSSION

Results of dc electrical conductivity in the temperature range of measurement and thermal activation energies of Schiff base compound (SB)



SCHEME 2 Molecular Configuration of (OPSB)

and organophosphorus Schiff base (OPSB) are given in Table (II). They were consistent with the values of semiconductors [7]. The plot of ln σ (σ = conductivity) versus 1/T of investigated compounds are shown in Figs (1&2). As investigated according to the solid state theory, the yielded straight lines over the given temperature ranges obeyed the Arrhenius dependence equation:

$$\sigma = \sigma_0 \exp(-E/kT),$$

where σ_0 is a constant, E is the conduction energy gap, and k is Boltzmann constant [8]. The total conductivity of a semiconductor as expected is ascribed to both intrinsic and extrinsic conduction, following this equation [9]:

$$(\text{Total conductivity})\sigma = \sigma_0 \exp(-\Delta E/2kT) + \sigma_{0_{(ex)}} \exp(-\Delta E/2kT)$$

It is suggested that the observed two regions of conduction associated with both (SB) and (OPSB) as shown in Figs (1&2) are due to (a) intrinsic conductance, and (b) extrinsic conductance and are depending on ΔE and $\Delta E_{(ex)}$ (ΔE_D or $\Delta E_A < \Delta E$) where ΔE is the forbidden gap width, ΔE_A: acceptor/valence band separation and ΔE_D: donor/conduction band separation. It is observed that the electrical conductivity and thermal activation energy of SB are consistent with that of the other aromatic Schiff bases e. g., benzylidene aniline ($\Delta E = 2.88$ eV, σ (100°C) 1.3×10^{-12} (ohm^{-1} cm^{-1}) and Salicylidene-aniline ($\Delta E = 3.28$ eV, σ (100°C) 2.7×10^{-11} (ohm^{-1} cm^{-1}) [10]. This comparison threw light of the importance of the chemical structure for conduction mechanism of the investigated compounds. Conductivity of the investigated SB (of the order $10^{-9}\ \Omega^{-1}\ \text{cm}^{-1}$)

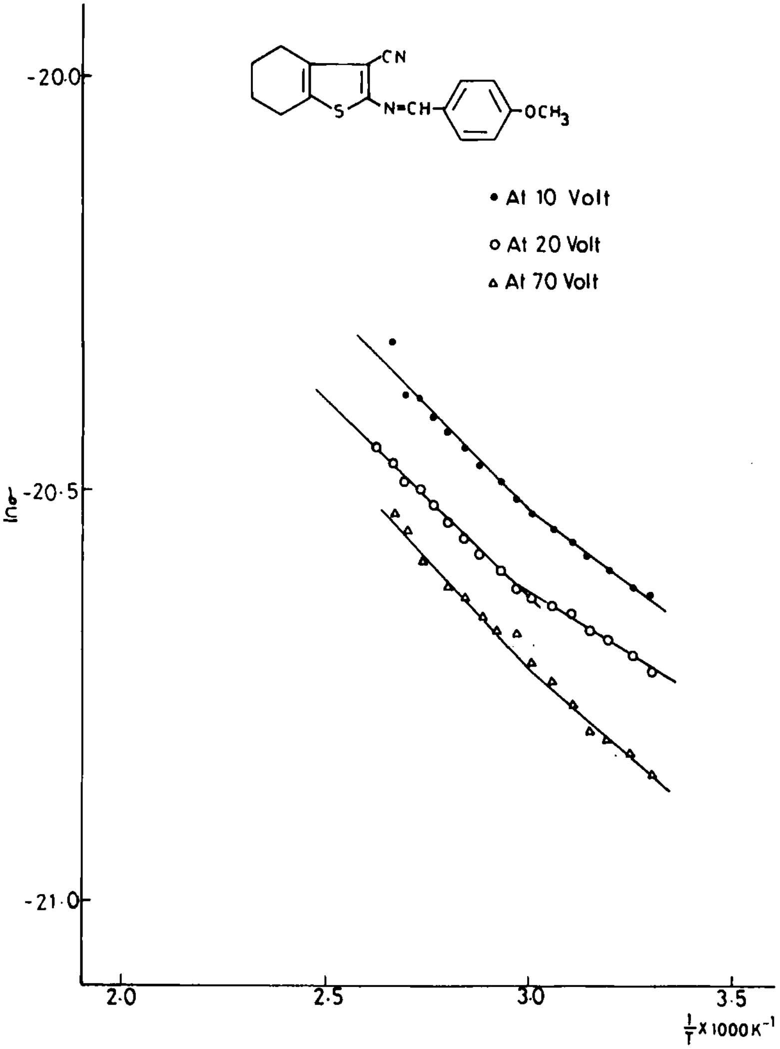


FIGURE 1 The relation between ln σ and reciprocal of absolute temperature 1/T for the Schiff base (SB)

are higher than those of the published Schiff bases (of the order 10^{-11} and 10^{-12} $\Omega^{-1}\text{cm}^{-1}$ respectively)[7] and of ordinary materials such as naphthalene and anthracene (of the order 10^{-20} $\Omega^{-1}\text{cm}^{-1}$) [11]. This is ascribed to the high conjugation that increase the delocalized π-electron along the molecular frame and decrease the energy gap between the ground state and the nearest allowed excited state as well as the increase in the basicity of the nitrogen atom of the azomethine group to some extent which participate in the conduction processes in the temperature range of measurements. Data of the electronic absorption spectral analysis also provide support for the mechanism of conduction processes taking place in the SB and OPSB. The calculated energy gaps corresponding to the maximum absorption wavelength in UV region in SB [λ_{max}.: 210, 276, 316 nm (ΔE: 5.9,4.5 and 3.9 eV respectively)] and OPSB [λ_{max}.: 210, 248, 264, 302 and 316 nm (ΔE: 5.9, 5.04, 4.7, 4.1, and 3.9 eV respectively] have been confirmed the observed two pathways of conduction processes in both. They are due to the generation of charges of all allowed $n\pi^*$ electronic transitions of the lowest excited energy states at low temperature range which participate in the first stage of conduction. On the other hand the admixed electrons of the $n\pi^*$ and $\pi\pi^*$ transitions contribute in second stage of conduction processes at higher temperature phase.

TABLE II Values of the electrical conductivity (σ) and the Activation Energies E_I, E_2^*

Sample	*Applied Voltage (Volt)*	T_c^* *(K)*	E_I^a *(eV) low*	E_{II}^a *(eV) high*	$\sigma_{low} \times 10^{-9}$ *at 303 K* $(\Omega^{-1}\ cm^{-1})$	$\sigma_{high} \times 10^{-8}$ *at 373 K* $(\Omega^{-1}\ cm^{-1})$
(SB)	10	333	0.034	0.0425	1.12	0.139
	20	338	0.026	0.0425	1.01	0.126
	70	337	0.038	0.042	0.886	0.119
(OPSB)	10	353	0.028	0.05	1.04	0.129
	20	358	0.023	0.049	0.88	0.105
	70	345	0.021	0.032	0.80	0.0944

a. E_I, E_{II} are the activation energies at the low and high temperatuer ranges respectively.

Infrared spectra Fig (3) indicate ν C=N bonds in conjugation with C=C of both benzene and thiophene rings attached with azomethine group at 1600, 1585 cm^{-1} and 1600 and 1590 cm^{-1} for SB and OPSB respectively. This conjugation decrease the energy gap between the valence state and

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* T_c is the transition temperature.

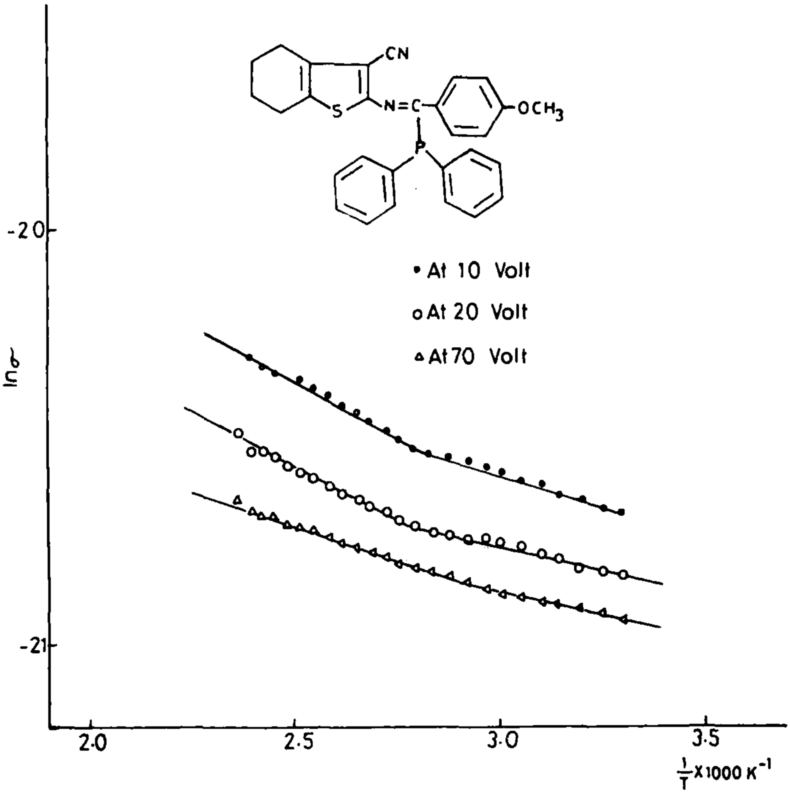

FIGURE 2 The relation between ln σ and reciprocal of absolute temperature 1/T for the Diphenyl phosphinyl Schiff base (OPSB)

next allowed lowest excited state to some extent which explain the relatively high conductivity of SB and OPSB. The conductivity of SB is higher than that of the OPSB is expected due to the high basicity of the nitrogen atom of azomethine group and the lower ionization energy of the lone pair electrons on the nitrogen atom of SB thus facilitate the releazing of electrons participating in the conduction processes in the temperature range of measurement. On the other hand the decrease of conductivity of OPSB than SB can probably be ascribed to the free rotation of the phenyl groups of diphenylphosphinyl group which is opposing a delocalization of the π electrons, as to the influence of the electrode materials [12]

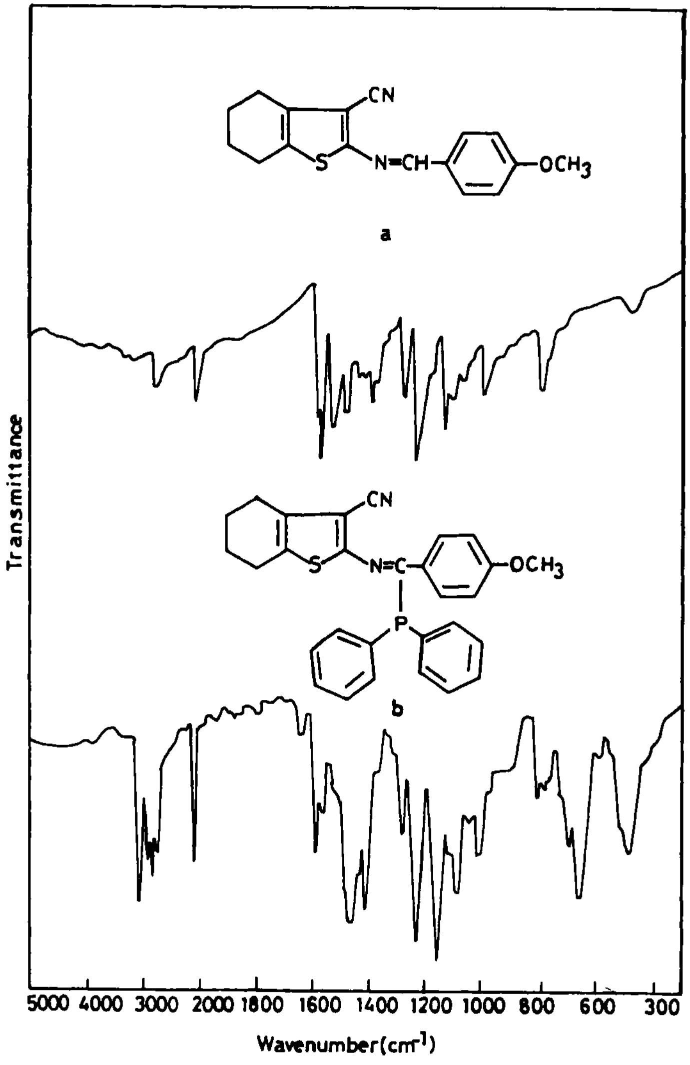

FIGURE 3 IR spectra of (SB) and (OPSB)

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