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Temperature dependence of the electrical conductivity in 4, 4′ bis(2-thenylideneamino)biphenyl and 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino)biphenyl compounds

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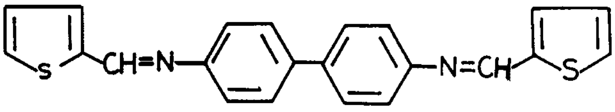
Correlation of the molecular structure and utilizing measurements of the electrical conductivity, activation energy of conduction of 4, 4′ bis(2-thenylideneamino)biphenyl (SB) and 4, 4′ bis(thenyl-diphenylphosphinylmethyleneamino)biphenyl (OPSB) compounds have been carried out. The results of the activation energies, obtained from the electrical conductivity measurements, as well as the energy gaps calculated from ultraviolet (u.v.) and visible spectra in the solid state indicate that the investigated compounds behave like semiconducting materials. The delocalized π-electrons in addition to the lone pairs of electrons on the nitrogen atoms of the two compounds as well as the donor effect of diphenylphosphinyl groups of OPSB compound were considered as the main sources participating in the conduction processes. *© 1999 Kluwer Academic Publishers*

1. Introduction

In the last decades great attention has been devoted to relating the chemical structure of inorganic and organic compounds to their electrical properties [1–5]. Attempts to investigate the electrical conductivity as well as the dielectric constants of a number of important classes of compounds involve the azomethine linkage (>C=N-), the oximes (>C=N-OH), the hydrazones (>C=NNH_2), and the azines $(>C=N)_2$ and relating these properties to the chemical structure have been carried out [1, 6]. As the electron system of these compounds is highly conjugated and is considered to be delocalized, to some extent, they show semiconducting properties. In the present paper, 4, 4′ bis(2-thenylideneamino)biphenyl "Schiff base" (SB) and 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino)biphenyl "organo-phosphorus Schiff base" (OPSB) with azomethine linkage were chosen and an attempt is made to investigate the dependencies of the electrical conductivity (σ), infrared, ultraviolet and visible absorption spectra of these compounds on their chemical constitution. Also, the diphenylphosphinyl groups contributions in enhancement of the semiconducting properties of Schiff base have been reported.

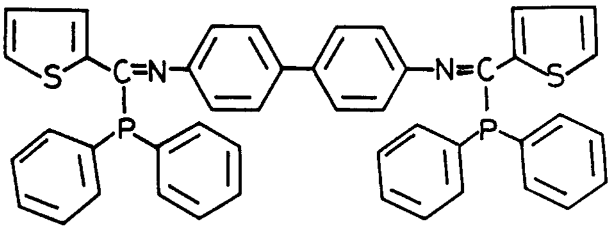
2. Experimental procedure

The chemicals used in this paper were of either Aldrich or BDH quality. 4, 4′ bis(2-thenylideneamino)biphenyl (SB) (scheme **I**) was prepared and purified as follows: A mixture of 2-thiophene carboxaldehyde (22 g, 0.2 M) and benzidine (19.4 g, 0.1 M) were heated in about 100 ml ethanol till boiling. The residue was cooled and the product was recrystallized from ethanol giving a yellow crystalline compound. On the other hand, the 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino) biphenyl (OPSB) (scheme **II**) was prepared as follows:



I

Scheme **I** Chemical structure of 4, 4′ bis(2-thenylideneamino)biphenyl.



II

Scheme **II** Chemical structure of 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino)biphenyl.

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A solution of diphenyl chlorophosphine was added to a well-stirred solution of the equimolar amount of 4, 4′ bis(2-thenylideneamino)biphenyl in the presence of triethylamine as a base in 100 ml dry dioxane. After complete addition, the reaction mixture was heated under reflux for 3 h. The solid formed, (triethylaminehydrochloride) was filtered off and the filtrate was evaporated in vacuum giving 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino)biphenyl 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 analyses Fig. 1 were carried out at $28 \pm 0.1\,^{\circ}$C using a Shimadzu IR 440. u.v. and visible absorption spectra were recorded using a Perkin-Elmer lambda 3B. The d.c. electrical conductivity was measured 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 [7]. The samples were prepared as compressed disks at $\sim$4 t cm^{-2}, diameter 10 mm and thickness 1–2 mm, coated with silver paste (BDH) and checked for good contact.

3. Results and discussion

The electrical conductivity of Schiff base compound (SB) and organophosphorus Schiff base (OPSB), as well as the thermal activation energies are given in Table II. The results show that the investigated compounds can be conventionally considered as semiconductors [8]. As expected, according to the solid state theory, a plot of ln σ ($\sigma =$ conductivity) versus $1/T$, Figs 2 and 3 of the investigated compounds yielded straight lines over the given temperature ranges and obeys 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 the Boltzmann constant [9]. Figs 2 and 3 show different straight lines associated with different activation energies indicating the simultaneous existence of intrinsic and extrinsic conductivity [10]. The data of electrical conductivity and thermal activation energy are consistent with those of the other aromatic Schiff bases, e.g. benzylidene–aniline ($\Delta E = 2.88$ eV, $\sigma(100\,^{\circ}\mathrm{C})1.3 \times 10^{-12}$ Ω^{-1} cm^{-1}) and salicylidene–aniline ($\Delta E = 3.28, \sigma(100\,^{\circ}\mathrm{C})$ 2.7×10^{-11} Ω^{-1} cm^{-1}) [11]. These results, which link the conductivity of Schiff base compounds with

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

Compound	Colour	Solvent used for crystallization	m.p. °C	Chemical Analysis							
				% Calculated				% Found			
				C	H	N	P	C	H	N	P
SB	Yellow	Ethanol	148	71.0	4.3	7.5	–	71.1	4.6	7.1	–
OPSB	Pale Yellow	DMF	218	73.7	5.7	3.7	8.6	74.1	5.4	4.1	8.3

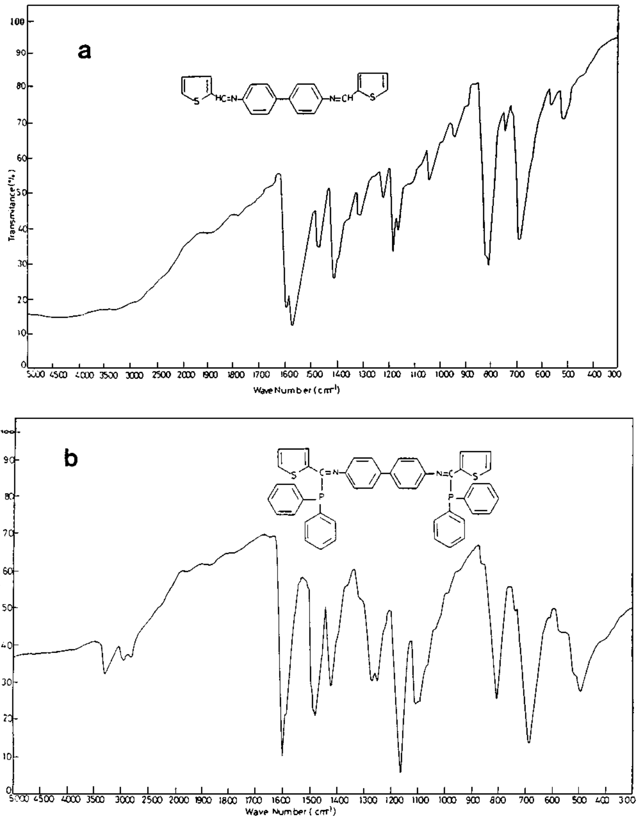

Figure 1 Infrared spectra of (a) 4, 4′ bis(2-thenylideneamino)biphenyl and (b) 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino)biphenyl.

TABLE II Values of the electrical conductivity (σ) and the Activation Energies E_I, E_{II}

Compound	Applied Voltage (V)	T_c^a(K)		E_I^b Low (eV)	E_{II}^b High (eV)	$\sigma_{low} \times 10^{-9}$ at 303 K (Ω^{-1} cm^{-1})	$\sigma_{high} \times 10^{-8}$ at 373 K (Ω^{-1} cm^{-1})
		I	II				
SB	10	348	358	0.026	0.049	0.48	0.057
	20	347	–	0.023	0.036	0.38	0.046
	70	333	353	0.006	0.042	0.43	0.047
OPSB	10	351	–	0.06	0.57	2.3	1.00
	20	340	–	0.14	0.68	1.3	1.57
	70	347	–	0.09	1.02	0.85	1.64

T_c^a is the transition temperature.
E_I^b, E_{II}^b are the activation energies at the low and high temperatures, respectively.

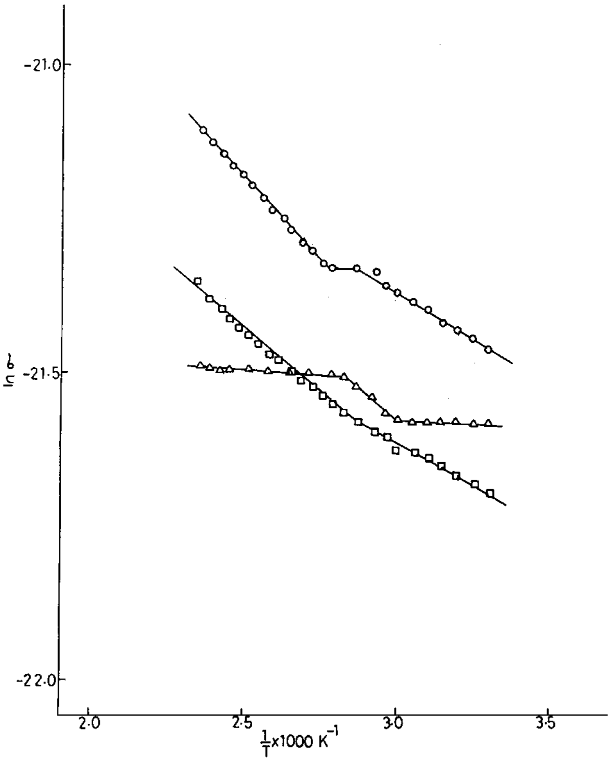

Figure 2 The relation between $\ln\sigma$ and $1/T$ of 4, 4′ bis(2-thenylideneamino)biphenyl at 10 V (O), 20 V (□) and 70 V (Δ).

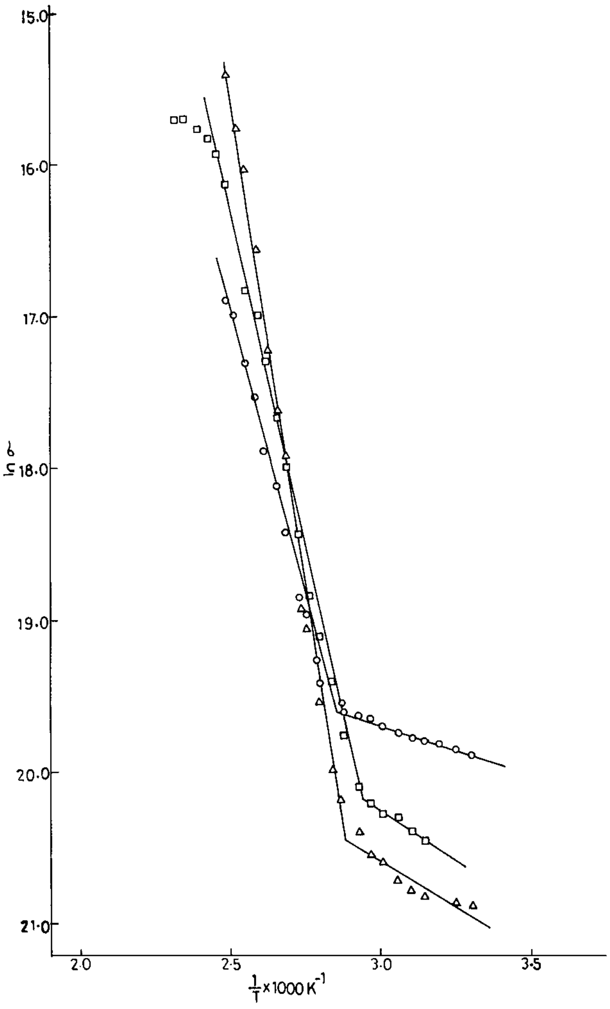

Figure 3 The relation between $\ln\sigma$ and $1/T$ of 4, 4′ bis(thenyldiphenylphosphinylmethyleneamino)biphenyl at 10 V (O), 20 V (□) and 70 V (Δ).

concepts used in classic organic chemistry, give some idea of the importance of the chemical constitution for conduction process in the investigated compounds. The higher conductivity of the Schiff base scheme (**I**) (of the order 10^{-9} Ω^{-1} cm^{-1}) compared to those of the published Schiff bases (of the order 10^{-11} and 10^{-12} Ω^{-1} cm^{-1} respectively) [11], and ordinary materials such as naphthalene and anthracene (of the order of 10^{-20} Ω^{-1} cm^{-1}) [12], is attributed to the high conjugation that increases the declocalized π-electrons participating in the conduction process. Infrared spectral studies Fig. 1 indicate unsaturated C=N bonds in conjugation with C=C bonds of both benzene and thiophene rings at 1620, 1565 cm^{-1} and 1600, 1575 cm^{-1} for both SB and OPSB, respectively. This lowers the energy gap between the valence state and the next allowed energy state and could interpret the relatively high conductivity of SB and OPSB. On the other hand, the conductivity of the SB is attributed to the ionization energy of the lone pair electrons on the nitrogen atoms which contribute in the conduction process particularly at the second regime of conduction at high temperature range (Fig. 2). The resulting conductivities of OPSB (scheme **II**) are higher than those of SB, see Table II. This increase is attributed to the donor effect of the diphenylphosphinyl groups on the Schiff base (SB) skeleton where it decreases the ionization energy of the lone pair of electrons on the nitrogen atoms to some extent thus facilitating the liberation the electrons participating in the conduction processes. Also, this increase can be understood if it is assumed that the interaction of the phosphorus orbitals with the butadiene-like π-MOs of the thiophen systems gives rise to the formation of new orbitals which are delocalized over the entire molecular structure of the OPSB (scheme **II**). The electrical conduction processes in both the SB and OPSB could thus be explained on the basis of data of the electronic transition energies within the molecules under investigation. Important work on the electronic absorption spectra of the two compounds in the solid phase has confirmed the observed two pathways of conduction processes in both. Through the first pathway, charges of all $n \rightarrow \pi^*$ electronic transitions which absorb at 281 nm and 291 nm for SB and OPSB, respectively, are associated with less activation energies and thus able to participate in the first regime of conduction processes at low temperature range. The second pathway of conduction at higher temperature phase can be attributed to all $\pi\pi^*$ transitions associated with absorption bands at 205 nm and 217 nm of SB and OPSB, respectively.

The excited states and the dielectric constants of the investigated compounds are now under further investigation, and more details will be published later. In conclusion, one can safely say that in the high-temperature region the possibility of overlapping between phosphorus orbitals and π-MOs of thiophen systems, as well as the donor effect of the diphenyl phosphinyl groups increases the conductivity values compared to those obtained in the low-temperature region.

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