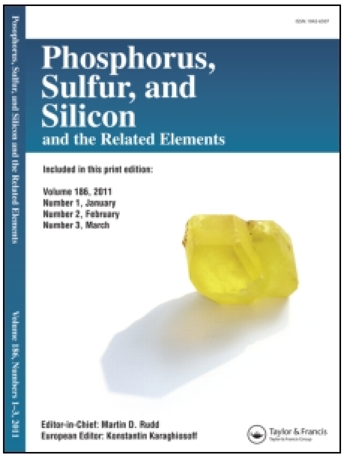

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STRUCTURAL AND ELECTRICAL CONDUCTIVITY STUDIES ON 1,4 BIS (P-METHOXYBENZILIDINE) (SB) AND ITS DIPHENYL PHOSPHINE DERIVATIVE (OPSB)

R. S. Farag[a]; B. A. El-Sayed[a]; M. A. El-Nawawy[a]; S. M. Shaaban[a]
[a] Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt

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STRUCTURAL AND ELECTRICAL CONDUCTIVITY STUDIES ON 1,4 BIS (P-METHOXYBENZILIDINE) (SB) AND ITS DIPHENYL PHOSPHINE DERIVATIVE (OPSB)

R. S. Farag, B. A. El-Sayed, M. A. El-Nawawy,
and S. M. Shaaban
Chemistry Department, Faculty of Science,
Al-Azhar University, Cairo, Egypt

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Schiff base "1,4 bis (p-methoxybenzilidine) benzene" (SB) and its diphenyl phosphine derivative (OPSB) have been isolated in solid state and characterized on the bases of macroanalytical, infrared IR, electronic and ^{1}H NMR spectral data, and thermal gravimetric analysis (TGA).

The electrical conductivity as a function of temperature for the two compounds under investigation (SB and OPSB) have been measured. The results of the electrical conductivity (σ), thermal activation energies associated with the electrical conductivity, as well as energy gaps calculated from the electronic absorption spectra in the solid state were consistent with those of the traditional semiconductors.

Keywords: Electrical conductivity; electronic; ^{1}H NMR; IR; organophosphorus compounds

INTRODUCTION

The synthesis of Schiff bases has been reported, and its coordination chemistry has been a subject of intensive study.[1–7] Little is known about the reaction of Schiff bases with halogenated organophosphorus compounds.[8,9] Also, recent work has produced useful study on the synthesis of phosphate and phosphine Schiff-base complexes.[10,11]

Attempts have been devoted to relating the electrical conductivity, as well as dielectric constants of a number of important classes of compounds involved the azomethine linkage ($\rangle$C=N—), the oximes

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Address correspondence to B. A. El-Sayed, Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt. E-mail: badr_elsayed@hotmail.com

$(>\mathrm{C{=}N{-}OH})$, the hydrazones $(>\mathrm{C{=}NNH_2})$ and the azines $(>\mathrm{C{=}N})_2$, to their chemical structures, where the electron system of these compounds is highly conjugated and considered to be delocalized to some extent. Thus, they show semiconducting properties.[12–17] El-Sayed et al. investigated the dependencies of the electrical conductivity (σ), infrared, ultraviolet, and visible absorption spectra of some Schiff-base compounds and their diphenyl phosphinyl derivatives on chemical constitution.[18,19] In the present work 1,4 bis (p-methoybenzilidine)-benzene (SB) and its diphenylphosphine derivative (OPSB) have been isolated in solid state and characterized. The electrical conductivity (σ) as a function of temperature for SB and OPSB showed semiconducting properties.

EXPERIMENTAL

The chemicals used in this study were provided in a high-purity grade by Aldrich & BDH.

1,4 bis (p-methoxy denzilidine) benzene (SB) was prepared and purified as follows:

A mixture of p methoxy benzaldehyde (0.2 mole) and p-phenylenediamine (0.1 mole) were heated in about 100 ml of ethanol till boiling for a half hour. The residue was cooled and the product was recrystallized from ethanol to give a yellow crystalline compound SB with m.p. 130°C.

1,4, bis p-methoxy benzilidine diphenylphosphine methylene amino phenyl (OPSB) was prepared and purified as follows:

A solution of diphenyl chlorophosphine (0.2 mole) was added to a well-stirred mixture of 1,4 bis (p-methoxybenzilidine) benzene (SB; 0.1 mole) and triethylamine (0.2 mole) as a base in 100 ml of dry dioxane. After completing the addition, the reaction mixture was heated under reflux for 3 h. The solid formed (triethylamine hydrochloride) was filtered off, and the filterate was evaporated under vacuum to give a solid compound that was recrystallized from DMF to obtain a yellow crystalline compound OPSB (m.p. 210°C).

The prepared compounds SB and OPSB were checked by thin layer chromatography (TLC). Microanalyses of carbon, hydrogen, and nitrogen were carried using the Perkin-Elmer 2400 CHN elemental analyzer.

IR spectra were measured as a KBr pellets at $28 \pm 0.1^\circ$C using a Shimadzu IR 440, and the data were reported in cm^{-1}. The electronic spectra were recorded using Perkin-Elmer lambda 3B spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian EM 360 L-90 MHz spectrometer using DMSO d6 as a solvent.

The dc 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.[20] The samples were prepared as compressed disks at ~4 ton cm^{-2}, diameter 10 mm, and thickness 1–2 mm, coated with silver paste BDH, and checked several times for good contact.

TGA was measured from room temperature up to 600°C under heating rate 10°C/min. the data were performed using Shimadzu TGA-50 H.

RESULTS AND DISCUSSION

SB and OPSB were checked by TLC and identified on the bases of their elemental analysis (Table I).

IR spectra of compound SB (Figure 1) showed the characteristic v—CH=N— stretching vibration at 1566 cm^{-1} and a characteristic stretching frequency for paradisubstituted aromatic ring at 783 cm^{-1}, but the IR spectra of compound OPSB (Figure 1) showed the characteristic v—CH=N— stretching vibration at 1600 cm^{-1}. A band at 700 cm^{-1} characterized stretching frequency for phenyl rings that attached to the phosphorus atom.[21] The band at 1100 cm^{-1} is investigated to be stretching vibration of v P—C, and a band at 2708 cm^{-1} is due to the stretching vibration of v CH aromatic.

The electronic spectra of SB showed two characteristic bands: one at 325 nm is corresponding to n–π^*, and the other one at 260 nm is due to the π–π^* transition. On the other hand the spectra of OPSB showed two characteristic bands: one at 325 corresponds to n–π^*, and one at 262 nm corresponds to π–π^* transition of the π electron system of phenyl rings.

^{1}H NMR spectra of SB indicate the presence of the azomethine proton at $\delta = 8.3$ ppm (1 H,S), methoxy protons at $\delta = 3.9$ ppm (OCHs, 3 H,S), and para disubstitution aromatic protons as AB system at $\delta = 7.2$–7.8, $J = 0.7$ ppm. The ^{1}H NMR spectra of compound OPSB indicated

TABLE I Chemical Analysis and Melting Points of SB and the OPSB

				Chemical analysis							
		Solvent used for	m.p.	% Calculated				% Found			
Compound	Color	crystallization	(°C)	C	H	N	P	C	H	N	P
SB	Deep yellow	EtOH	130	77.2	6.1	10.6	—	77.4	5.8	11.5	—
OPSB	Yellow	D.M.F	210	62.1	4.5	5.8	5.5	62.4	4.8	5.5	5.8

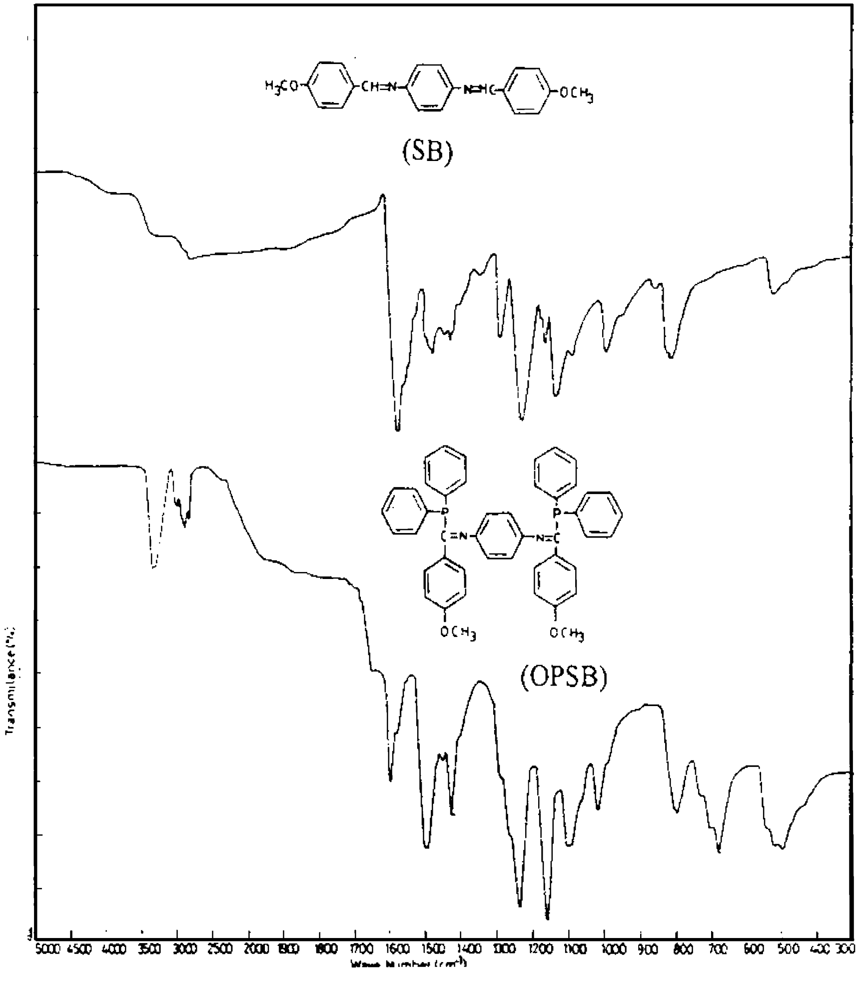

FIGURE 1 IR spectra of compounds (SB) and (OPSB).

the disappearance of the azomethine proton due to the replacement of the hydrogen atom by the diphenylphosphine group, the methoxy protons appeared at $\delta = 3.7$ ppm (OCHs, 3 H,S), and para disubstituted aromatic protons as AB system associated with the phenyl protons of diphenylphosphine group at $\delta = 6.7$–8.2 ppm.

The obtained data are in good agreement with those calculated for the suggested structure of the prepared compounds SB and OPSB.

The TGA thermograms of SB and OPSB compounds indicate two transition steps and residue due to decomposed products, where the

TABLE II Transitions of the TGA of SB and OPSB Compounds

Compound	Mol. wt.	m.p.	Transition, weighty, temperature		Residue %
SB	344	130	92.44% 290–400°C	6.63% 400–600°C	0.93
OPSB	712	210	33.45% 200–350°C	37.50% 350–600°C	29.05

residue is thermally stable up to 600°C as indicated in Table II and Figure 2.

The electrical conductivity (σ) of the SB and OPSB is measured up to a temperature near the melting point of each compound from room temperature. The variation of conductivity with temperature for the compounds is shown in Figures 3 and 4. The electrical conductivity

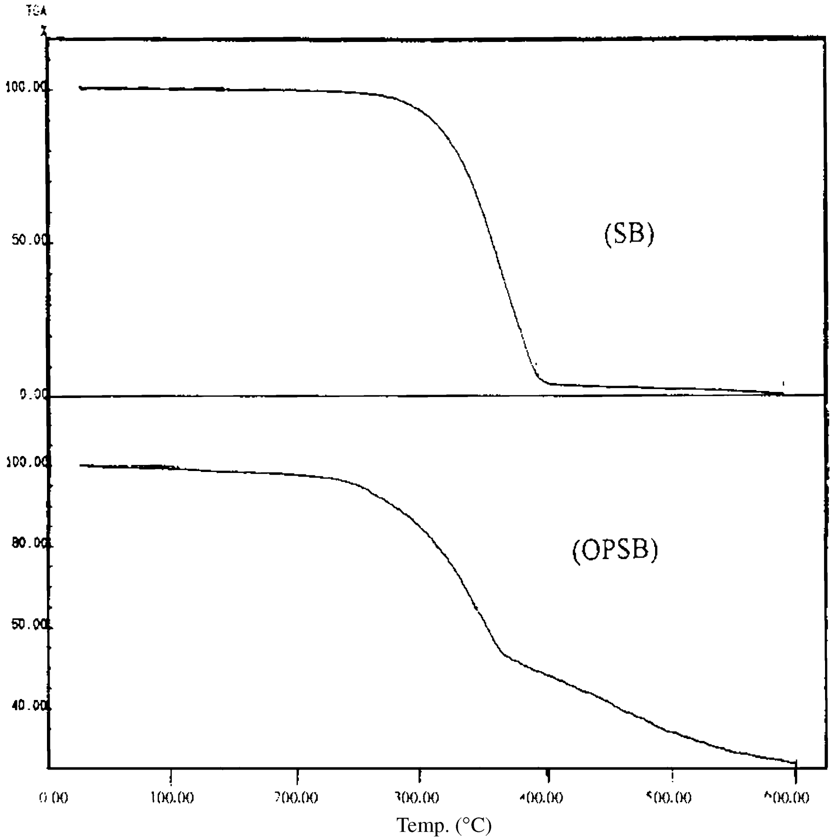

FIGURE 2 TGA diagram of (SP) and (OPSB).

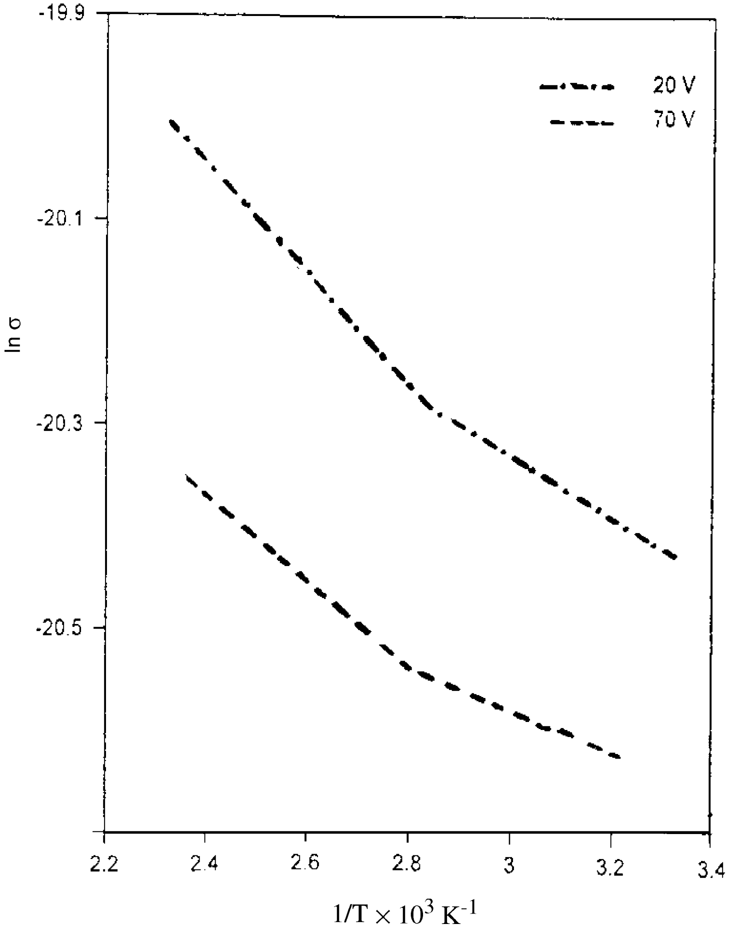

FIGURE 3 The relation between ln *a* and 1/T of (SB) at 20 V and 70 V.

values and the thermal activation energies for both compounds are given in Table III. In general, it has been well established from these values that they behaved as the traditional semiconductor materials, i.e., with (a) varying exponentially with temperature according to the following equation:

$$\sigma = (\sigma_0 \exp(-E/kT)) \tag{1}$$

where σ_0 is the pre-exponential factor and Ec is the activation energy of conduction. Equation (1) is illustrated by the Arrhenius plots of Figures 3 and 4, whose slopes give the different activation energies Ec listed in Table III. The different straight lines associated with different

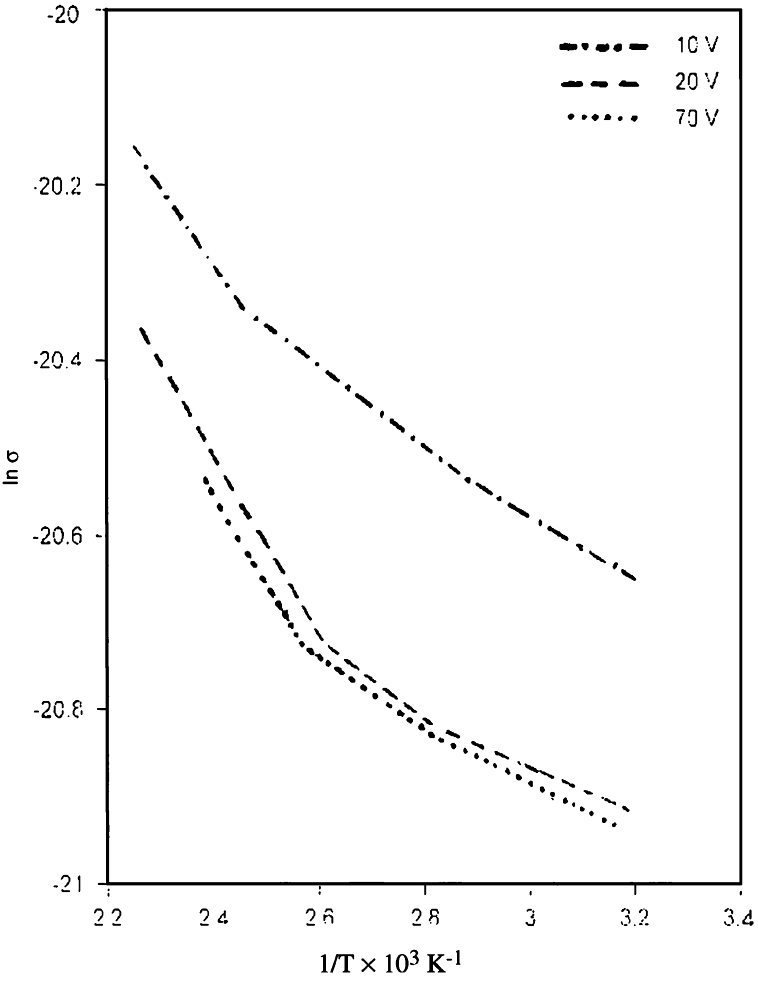

FIGURE 4 The relation between ln *a* and 1/T of (OPSB) at 10 V, 20 V, and 70 V.

activation energies indicated the simultaneous existence of intrinsic and extrinsic conductivity (Equation (1)). The conductivity of the SB and OPSB at room temperature is in the range of 0.79–1.39 × 10^{-9} Ω^{-1}. The variation of conductivity with temperature for both SB and OPSB can be divided into two regions. These two regions of conduction processes could be explained on the basis of their electronic transition energies within the molecules in the solid state. Through the first region of conduction at low temperature range the generation of charges of all allowed n–π^* electronic transitions of the lowest excited states, which

TABLE III Values of the Electrical Conductivity (σ) and the Activation Energies E_I and E_{II}

Sample	Applied voltage (Volt)	T_c^a(K) I	T_c^a(K) II	E_I^b(eV) low	E_{II}^b(eV) high	$\sigma_{low} \times 10^{-9}$ at 303 K(Ω^{-1}cm^{-1})	$\sigma_{high} \times 10^{-8}$ at 373 K(Ω^{-1}cm^{-1})
SB	10	361	—	0.0255	0.05	1.37	0.171
	20	361	—	0.0255	0.05	1.39	0.170
	70	361	—	0.0210	0.035	1.11	0.128
OPSB	10	403	—	0.0420	0.0765	1.07	0.131
	20	361	392	0.0420	0.079	0.799	0.0930
	70	388	362	0.0475	0.085	0.801	0.0935

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

absorb at (λ_{max}: 325 nm) for both SB and OPSB, were associated with less activation energy (ΔE: 3.85 eV) and thus were able to participate in this region of conduction process. The second region of conduction at higher temperature range could be attributed to the admixed electron of the n–π^* and π–π^* transitions that absorb at (λ_{max}: 260 nm and 262 nm), which were associated with higher activation energies (ΔE: 4.80 eV and 4.77 eV) for SB and OPSB, respectively.

The higher conductivity of the SB (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},[22] and ordinary materials such as naphthalene and anthracene (of the order 10^{-20} Ω^{-1} cm^{-1}),[23] is attributed to the high conjugation within the molecular system that increases the delocalization of π electrons participating in the conduction process. Infrared spectral studies (Figure 2) indicate unsaturated C=N bonds in conjugation with C=C bonds of benzene rings at 1566 cm^{-1} and 1600 cm^{-1} for SB and OPSB, respectively. This lowers the energy gap between the valence state and the next allowed energy state and might explain the relatively high conductivity of SB and OPSB. The greater decrease of conductivity of OPSB, as compared to SB, with elevated temperature 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.[14]

REFERENCES

[1] P. V. Rao, N. R. Rao, V. J. Tyagaand, and M. C. Ganorkar, *Indian J. Chem. Sec. A*, **25**(5), 482 (1985).

[2] T. M. Aminabhavi, N. S. Biradar, and M. C. Divarar, *Indian J. Chem. Sec. A*, **25**(3), 482 (1986).

[3] M. T. H. Tarafldar, *Indian J. Chem. Sec. A*, **28**(6), 531 (1989).

[4] A. J. Blake, J. M. Mcinnes, P. Mountford, et al., *J. Chem. Soc. Dalton Trans.*, **379,** (1999).

[5] L. Long, S. Yang, Y. Tong, et al., *J. Chem. Soc. Dalton Trans.*, 1999.

[6] S. Shama and H. Omara, *Spectroscopy Lett.*, **34,** 1 (2000).

[7] N. T. Madhu and P. K. Radharkrishnan, *Synth. React. Inorg. Met.-Org. Chem.*, **31**(2), 339 (2001).

[8] S. Nurtdinov, Kh-in Khim Tekhnol Inst Kazan VSSRZh. Obsch.Khim51 (7) (1981) 1549–1553 Ca 96 (1982) 20177.

[9] I. M. Abd-Ellah, E. H. M. Ibrahim, and R. S. Farag, *Gazzatta Chimica Italiana*, **118,** 141–143 (1988).

[10] I. M. Abd-Ellah, E. H. M. Ibrahim, and R. S. Farag, *Ind. Sci. Acad.*, **53A**(6), 736–744 (1987).

[11] I. M. Abd-Ellah, A. N. Khazendar, and R. S. Farag, *Proc. Ind. Natn. Sci. Acad.*, **55A**(4), 678–682 (1989).

[12] B. A. El Sayed, S. M. Shaban, M. M. Sallam, and A. A. A. Emara, *J. Mater. Sci. Lett.*, **15,** 883 (1996).

[13] B. A. El Sayed, M. M. El Desoky, S. M. Shaban, and A. B. Sayed, *J. Mater. Sci. Mater. Electr.*, **3,** 124 (1992).

[14] M. B. El Sayed, *J. Phys. Chem. Solids*, **53,** 1041 (1992).

[15] J. Koch and M. Hanack, *Chem. Ber.*, **116,** 2109 (1983).

[16] G. Kossmehl, *Ber. Bunsenges. Phys. Chem.*, **83,** 417 (1979).

[17] B. A. El-Sayed, S. M. Abdel Wahab, A. M. El-Refae, and K. A. Darwish, *J. Mater. Sci. Lett.*, **15** (1996).

[18] B. A. El-Sayed, M. A. Nawawy, E. M. Abd-Ellah, and R. S. Farag., *J. Mater. Sci.*, **34,** 2715–2718 (1999).

[19] B. A. El-Sayed, E. M. Abd Ellah, M. A. El-Nawawy, and F. M. Al;-Azab, *Phosphorus Sulfur Silicon*, **157,** 57–65 (2000).

[20] M. A. Ahmed and F. A. Radwan, *J. Phys. Chem. Solids*, **49,** 1385 (1988).

[21] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23,** 853 (1951).

[22] T. Prot, *Roczmki Chem. [Ann. Soc. Chem. Polonorum]*, **43,** 2121 (1969).

[23] Y. Okamto, F. T. Huang, A. Goroon, W. Brenner, and B. Rubin, Organic semiconductors. In *Proceeding of an inter-Industry conference*, edited by J. J. Brophy and W. B. Jo.