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THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY OF DIAZADIPHOSPHETIDINE DERIVATIVES

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Abstract

The d.c. electrical conductivity measurements as a function of temperature of 2,2,2,4,4,4-hexachloro-1,3-bis(2-chlorophenyl)-1,3,2,4-diazadiphosphetidine, (HCCIDP), 2,2,2,4,4,4-hexachloro-1,3-bis(2-bromophenyl)-1,3,2,4-diazadiphosphetidine (HCBrdP), and 2,2,2,4,4,4-hexachloro-1,3-di-o-tolyl-1,2,4-diazadiphosphetidine (HCMDP) compounds have been carried out. The semiconducting properties of the investigated compounds were arising from electron delocalization via intramolecular interaction of p-electrons of (C=C) bonds and electron-donating groups in ortho positions. The conductivity was found to increase in the higher temperature range than in lower due to the trigonal bipyramidal structure which increases the possibility of electron delocalization and the interaction of p-electron system.

Keywords: DC conductivity; IR and UV spectra; diazadiphosphetidine derivatives

Introduction

The reactions of PCl_5 with aromatic and aliphatic amines have been investigated in some detail [1-4]. Recently the study of the relationship between electrical conductivity and chemical structure of inorganic and organic compounds has attracted increasing attention [5-8]. In the present work D. C. conductivity properties of new synthesized PCl_5 with o-bromoaniline, o-chloroaniline and o-toluidine and relating these properties to the chemical structure have been carried out.

Results and discussion

The d.c. electrical conductivity (σ_{dc}) of diazadiphosphetidine (DP) derivatives as well as the thermal activation energies is given in Table 1. The results show that the investigated compounds conventionally behave as semiconductive materials [9,10]. A plot of $\ln \sigma$ versus $1/T$, (Fig. (a)-(c) at applied voltages 5, 20 and 70 V (ohmic range) of DP derivatives yielded different straight lines over the given temperature range and obeyed the Arrhenius dependence equation,

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E}{KT}\right),$$

where σ_0 is a constant, E is the conduction energy gap and K is the Boltzmann constant [11]. As expected, according to the solid state theory, the activation energies associated with different straight lines (Fig. (a)–(c)) are due to the simultaneous existence of intrinsic and extrinsic conductivity following [11]

$$\sigma_{d.c} = \sigma_0 \exp(-\Delta E/2KT) + \sigma_{0(ex)} \exp(-\Delta E_{(ex)}/2KT)$$

where ΔE is the forbidden gap width and $\Delta E_{(ex)}$ (ΔE_D or $\Delta E_A < \Delta E$ where ΔE_D : donor/conduction band separation and ΔE_A : acceptor/valence band separation). The obtained electrical conductivity values and thermal activation energies (Table 1) are consistent with those of other biphenyl Schiff base (BPSB) and its organo-phosphorus derivative previously studied by El-Sayed et al. [12] ($\Delta E = 0.049$ eV, $\sigma(100^\circ\text{C}) = 0.58 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$) for BPSB and ($\Delta E = 0.57$ eV, $\sigma(100^\circ\text{C}) = 1 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$) for organo-phosphorus of BPSB. These results, which link the conductivity of HCDP compounds with concepts used in classic organic chemistry, give some idea of the importance of the chemical constitution for conduction process in the investigated compounds. The temperature-dependence component (J_{dc} has a very low activation energies (Table 1), this is convenient for applying a hopping mechanism similar to the conduction mechanism observed with impure silicon [13,14], that is characterized by a localization of the carriers between potential barriers; to overcome these barriers the carriers need an activation energy which causes the temperature dependence of the conductivity. The conductivity values of biphenyl derivatives (of the order $10^{-8} \Omega^{-1} \text{cm}^{-1}$) are high compared to those of ordinary organic materials such as naphthalene and anthracene (of the order of $10^{-20} \Omega^{-1} \text{cm}^{-1}$) [15]. This is attributed to the effect by incorporation of electron donor substituents and investigated the presence of extrinsic conduction. The d.c. characteristics of current (I) as a function of voltage (V) of DP derivatives were obtained (Fig. 3). The current was measured four times at any given applied voltage for the room temperature characteristics. The mean of these four readings was plotted against applied voltage magnitude and, for all the investigated compounds, yielded curves which were linear and agreed the Ohm's law.

The assignment of the IR absorption bands observed for diazadiphosphetidine (DP) derivatives, Fig. 3 showed that the particular vibrations noted, indicate the presence of (C=C) bonds of the two phenyl groups in conjugation along the molecular skeleton of each compound at 1575 cm^{-1} , 1638 cm^{-1} and 1614 cm^{-1} for

HCBrdP, HCCIDP and HCMDP, respectively. The characteristic bands corresponding to the P-N, PNP and P-Cl were collected in Table 2. This lowers the energy gap between the valence state and the next allowed energy state and could interpret the relatively high conductivity of DP derivatives. The resulting conductivities associated with HCBrdP and HCCIDP are higher than of HCMDP, see Table 1. Based on the molecular structure of DP derivatives Scheme 1 one can design the skeleton of the discussion on the conductivity results, where there is a relationship between the chemical structure (as well as the effect of the substituents) and the electrical properties. According to the previously proposed model [16,17], DP molecular structure undergoes a large conformational change upon excitation ($S_1 \leftarrow S_0$) and the inter-ring exciton interaction is large for the trigonal bipyramidal excited state [18,19]. Since the interaction of π electrons in a π system is maximal when the skeleton of the system is trigonal bipyramidal, one could expect the intramolecular interaction within the DP compounds is maximal in the excited state which gives possibility for increasing π electron delocalization at higher temperature range which is associated with higher conductivity values than those at low temperature range because at high temperature range the equilibrium geometry of diazadiphosphetidine (DP) is decreased with loss of planarity which facilitate the delocalization of π electrons within the molecules. As the system deviates from the trigonal bipyramidal geometry, at higher temperature range (S_1) down to the room temperature (S_0), the interaction of π electrons will be reduced to the corresponding extent and this explains the decrease of the electrical conductivity in the low temperature range. The mechanism of the conduction process of the investigated compounds may be understood under the light of UV and visible absorption spectral data as shown in Table 3.

Experimental

Synthesis of 2,2,2,4,4,4-hexachloro-1,3-bis(2-chlorophenyl)-1,3,2,4-diazadiphosphetidine, 2,2,2,4,4,4-hexachloro-1,3-bis(2-bromophenyl)-1,3,2,4-diazadiphosphetidine and 2,2,2,4,4,4-hexachloro-1,3-di-o-tolyl-1,3,2,4-diazadiphosphetidine (Scheme 1) were prepared by Abd-Ellah et al [4]. These compounds were checked by thin layer chromatography (TLC) and identified by elemental analysis before the electrical data were collected. Infrared (IR) spectra were recorded at $28 \pm 0.1^\circ\text{C}$ with a Unicam Analytical system, Mattson 1000 series FTIR spectrometer, as KBr mixed discs. Ultraviolet and visible absorption spectra

were recorded on a Unicam UV-vis spectrometer, as KBr discs. The d.c. conductivity of the samples was measured at a constant d.c. voltage using the potential probe method [20]. The sample temperature was measured using a calibrated nickel-chrome thermocouple in the range 300-400 K. The samples were prepared for the electrical conductivity (σ) as compressed discs at ~ 4 ton cm^{-2} , diameter 13 mm and thickness ~ 1.5 mm.

The two surfaces were polished, coated with silver paste (BDH, UK) and checked for good contact several times at elevated temperatures without any effect on the stability of the silver contacts. The apparatus employed in performing the electrical measurements has already been described [21], the most convenient sample holder which we have devised is pictured in Fig. 1.

Table (1): Values of the electrical conductivity (σ) and thermal activation energy of (HCBrdP), (HCCIDP) and (HCMDP).

Compound	Applied Voltage (V)	^a T _{CI} (K)	^a T _{CII} (K)	^b E _I (low) (eV)	^b E _{II} (eV)	^b E _{III} (high) (eV)	$\sigma_i \times 10^{-10}$ at 303 K ($\Omega^{-1}\text{cm}^{-1}$)	$\sigma_i \times 10^{-9}$ at 393 K ($\Omega^{-1}\text{cm}^{-1}$)
HCBrdP	5	336	362	0.072	0.087	0.178	4.061	4.467
	20	328	363	0.077	0.098	0.178	4.022	3.868
	70	333	366	0.073	0.098	0.176	3.989	2.335
HCCIDP	5	358	378	0.071	0.148	0.218	3.124	4.428
	20	359	372	0.076	0.124	0.216	3.168	3.789
	70	362	388	0.075	0.195	0.218	3.186	2.368
HCMDP	5	337	372	0.210	0.285	0.191	0.745	3.978
	20	333	353	0.218	0.298	0.191	0.725	3.367
	70	345	366	0.217	0.276	0.195	0.689	2.156

^aT_C is the transition temperature.

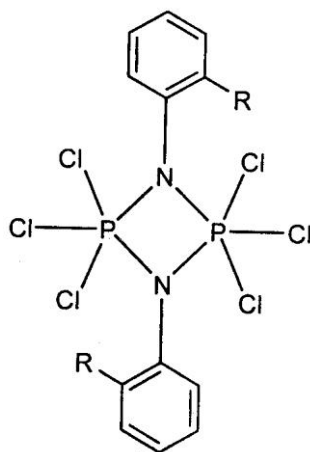
^bE_I, ^bE_{II} and ^bE_{III} are the activation energies at the low, medium and high temperature ranges, respectively.

Table (2): IR spectra of (HCBrdP), (HCCIDP) and (HCMDP).

Compound	ν_{PNP}	$\nu_{\text{disubstituted ring}}$	$\nu_{\text{p-N}}$	$\nu_{\text{P-Cl}}$
HCBrdP	972, 875	776 (m)	1254 (m)	458 (m)
HCCIDP	932, 827	775 (m)	1225 (m)	457 (m)
HCMDP	927, 832	770 (m)	1223 (m)	446 (m)

Table (3): Electronic absorption spectral data of HCBrdP, HCCIDP HCMDP compounds.

Compound	λ_{abs} (nm)	E_g (eV)
HCBrdP	234, 256, 277, 315	5.3, 4.8, 4.5, 3.9
HCCIDP	233, 255, 278, 314	5.3, 4.8, 4.4, 3.9
HCMDP	230, 254, 275, 312	5.4, 4.9, 4.5, 4.0



- (a) R = Br
 (b) R = Cl
 (c) R = CH₃

Scheme 1

Molecular configuration of ortho diazadiphosphetidine derivatives: (HCBrdP), (HCCIDP) and (HCMDP)

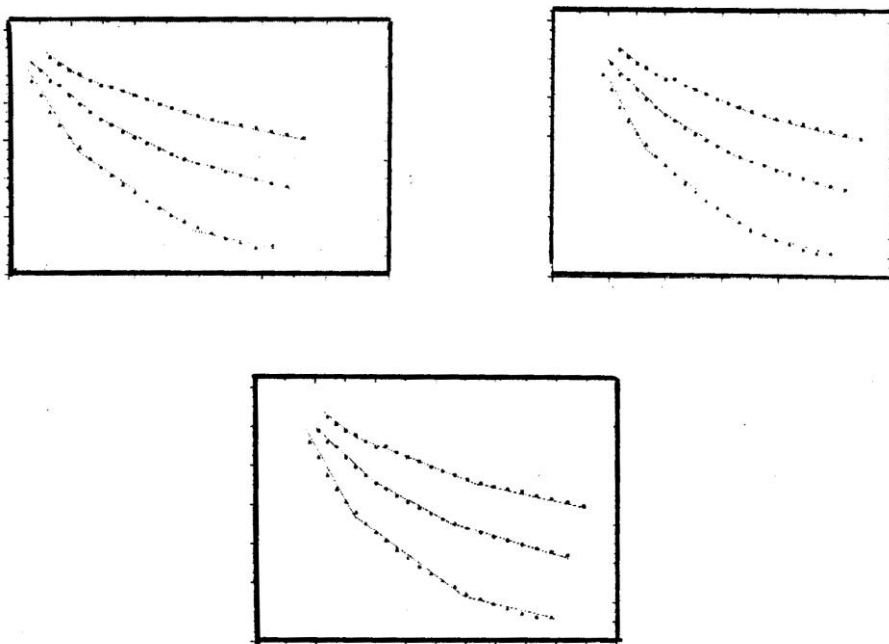


Fig. (1): The relation between $\ln s$ and the reciprocal of the absolute temperature $1/T$ at (■) 5V, (●) 20 V and (▲) for the (a) (HCBrdP), (b) (HCCIDP) and (c) (HCMDP), respectively.

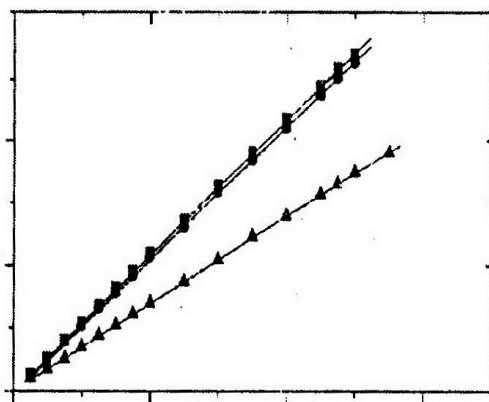


Fig. (2): Current-Voltage characteristics for (■) (HCBrdP), (●) (HCCIDP) and (▲) (HCMDP) at room temperature, respectively.

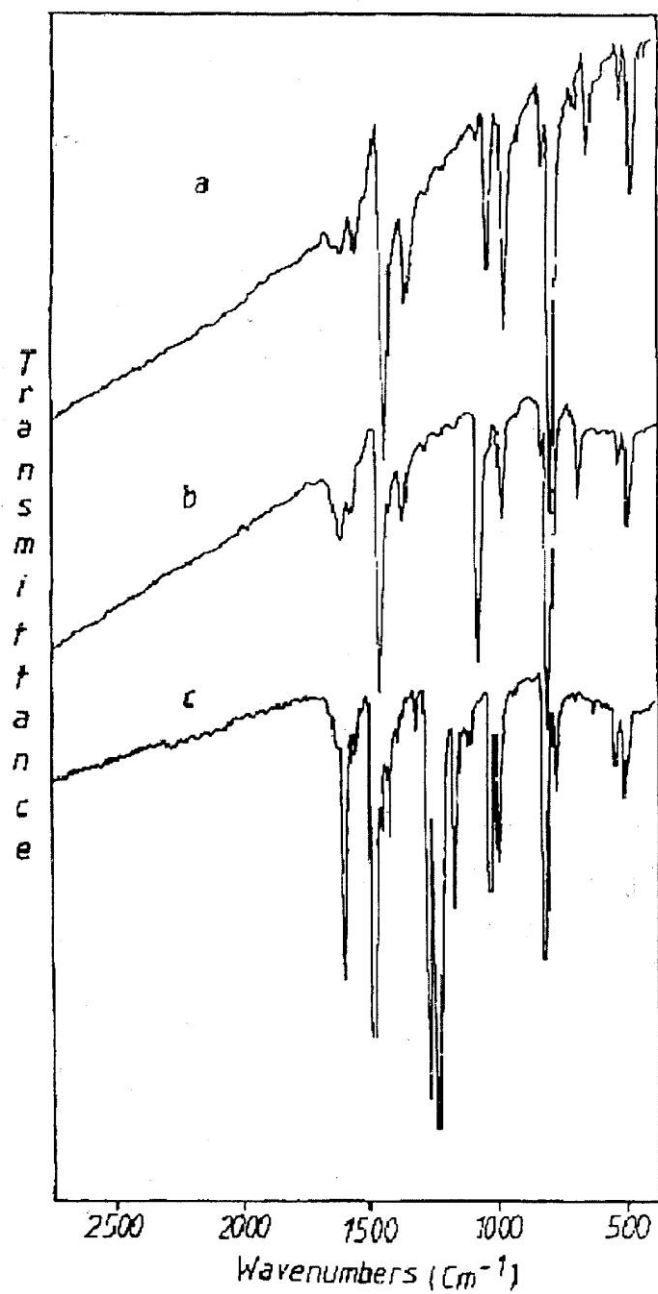


Fig. (3): IR spectra of the (a) (HCBrdP), (b) (HCCIDP) and (c) (HCMDP).

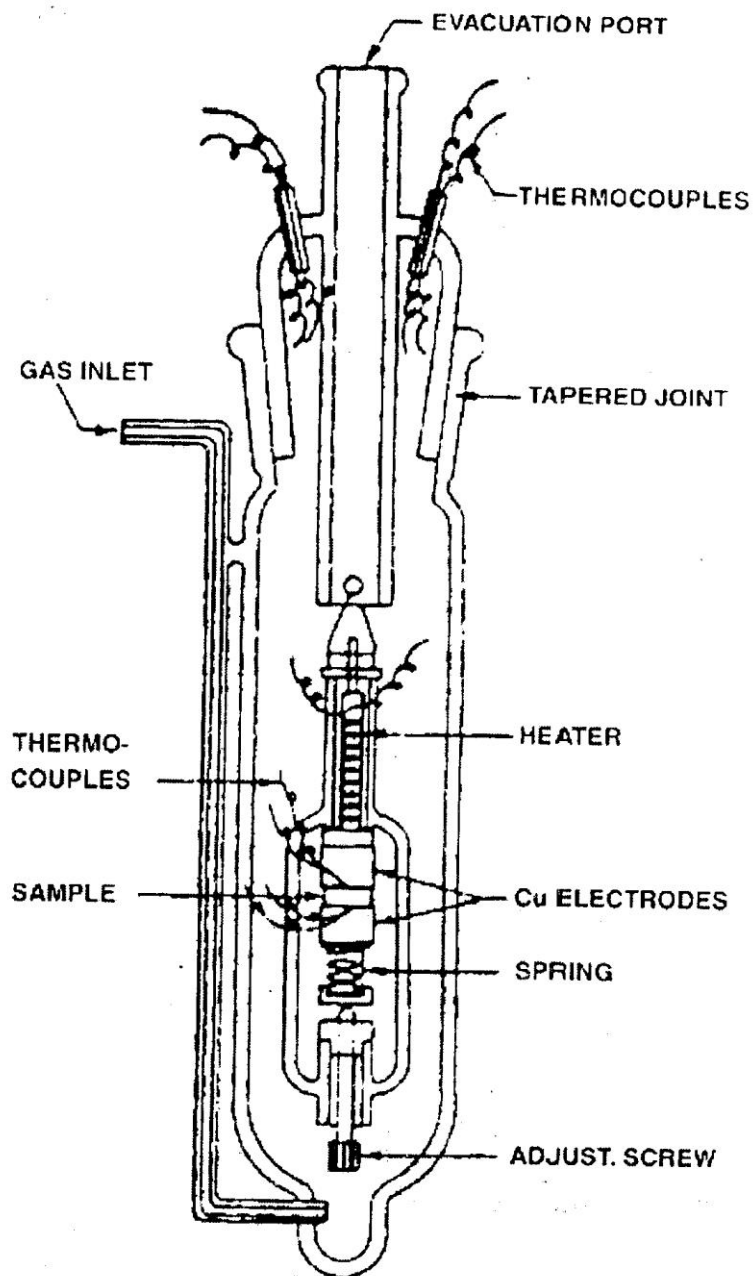


Fig. (4): Sample holder

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