Thermal Degradation And Solid State Electrical Conductivity Study Of Phenothiazinium Picrates

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ABSTRACT

Temperature dependent electrical conductivity and thermal degradation kinetics of charge transfer complexes of phenothiazine derivatives namely promethazinium picrate(PP), dioxo promethazinium picrate(DPP), promazinium picrate(PMP) and chlorpromazinium picrate(CPP) are reported. The activation energies are calculated based on their electrical conductivity studies conducted over the temperature range 30-175^{0}C. These energies for promethazinium, dioxo promethazinium, promazinium and chlorpromazinium picrates are found to be 0.19, 0.52, 0.17 and 1.29eV respectively. DPP and PMP exhibited semiconducting behavior whereas PP and CPP showed both metallic and semiconducting behaviors. Single crystal X-ray data of PMP and CPP are presented. The materials are analyzed for the kinetic parameters like the activation energy for decomposition and the Arrhenious pre-exponential factors in their pyrolysis region using Broido's, Coats-Redfern and Horowitz-Metzger methods. Using these factors and the standard equations thermodynamic parameters such as enthalpy, entropy and free energies are calculated. Thermogravimetric study on these phenothazine picrate derivatives in air indicated that they are thermally stable up to100^{0}C. © 2007 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Phenothiazine derivatives substituted in 2 and 10 positions belong to a big group of tricyclic aromatic compounds. They are in extensive use in psychiatry as traquilizers and neuroleptics. Due to their characteristic structure they exhibit many valuable and interesting properties. Eversince the discovery of semiconducting properties of phenothiazine, a lot of attention has been paid to improve the material properties of these derivatives. The first synthesis of phenothiazine was reported by Bernthsen in the year 1883, since then, many significant results have been reported which are of interest not only for the workers in the field of phenothiazines but also for the entire heterocyclic chemistry[1]. Now phenothiazines are widely known for their important pharmacological actions[2-5]. Phenothiazine and its derivatives are excellent electron donars[6-7]. The donar activity of phenothiazine is so high that even in the ground state there is practically the total transfer of electron to an acceptor with the formation of charge-transfer(C-T) complexes.

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These C-T complexes form a new class of organic electronic materials. Charge transfer materials have provided a lot of scope for the researchers worldwide for replacing conventional inorganic electronic materials[8-9]. Slifkin and Allison have reported the ionization potentials of a few condensed ring aromatic hydrocarbons and the maximum absorption of their C-T complexes with chloranil in carbon tetra chloride[10]. Bhat and Rao have studied solid state C-T complexes of benzidiene-iodine, p-phenylene diamine-iodine, phenothiazine-iodine as well as antimony chloride[11]. Solid-state electrochemical cells have been devised using a variety of metals as anodes and electronically conducting C-T complexes as cathodes by Gutmann et al.[12]. Pampallona et al. have also studied C-T complexes as electrodes in solid state cells[13]. They have stated that iodine-phenothiazine and iodine-N-methyl phenothiazine offer excellent prospectus for use as iodine electrodes in solid state cells. Jayarama et al. have investigated the reaction of few phenothiazines with nitroso-R salt[14,15]. Zakhari et al. have reported the interaction between chloranilic acid and phenothiazine[16]. Berges et al. have reported electrical conductivity and dielectric relaxation of phenothiazine-tetracyano ethylene 1:1 complex[17]. Singh et al. have studied molecular semiconductors based on phenothiazine tetra cyano ethylene and phenothiazine 2,3dichloro-5,6dicyano-p-benzoquinone C-T complexes[18,19]. Tarasiewics and Puzanowska-Tarasiewics have used picric acid for the colorimetric determination of phenothiazine derivatives[20]. Tarasiewicz and Basinska have reported the analytical applications of chlorpromazinium picrate[21]. The charge-transfer complexes of phenothiazine derivatives promethazine, promazine, chlorpromazine and dioxopromethazine with picric acid have been studied by using UV-Visible, IR, NMR and room temperature electrical conductivities[22]. However, a thorough literature survey revealed that temperature dependent electrical conductivity, and thermal degradation studies on the above phenothiazinium picrate derivatives have not been done. In addition, except in the case of PP, single crystal study has not been done for the other three picrate derivatives. Obtaining single crystal DPP is not successful so far. Single crystal X-ray data of PMP and CPP are presented here[23,24]. The present study is hoped to throw more light on the thermal degradation and electrical conductivity properties of phenothiazinium picrate derivatives, which may help for the more judicial choice of these materials for the construction of suitable electronic devices.

RESULTS AND DISCUSSIONS

The elemental analysis of all the phenothiazine picrate derivatives for carbon, hydrogen, nitrogen and sulphur agreed very well with the theoretical values, indicating the high purity of the samples. The UV-Visible spectra of PP, PMP and DPP are recorded in alcohol medium, whereas spectrum of CPP is recorded in acetonitrile medium. The absorption peaks due to picric acid are observed at 370-374nm in alcohol/acetonitrile media in comparison of the data at 340-348nm in chloroform. The bathochromic shifts observed are expected due to $\pi_{NO2}^* \rightarrow \pi_{NO2}^*$ transitions in the presently used more polar solvent. Further, the charge-transfer absorption peaks are observed as shoulders which are not as clearly visible observed at 394-396 nm in comparison to the earlier values reported in chloroform solvent at 402-406nm. Hypsochromic shifts confirm further, due to the $n_{PD} \rightarrow \pi_{NO2}^*$ C-T transitions, where PD stands for phenothiazine derivative. The wavelength of maximum absorption and log ε values agreed well with the earlier reported values[20,22]. The IR spectral studies on the phenothiazine picrate derivatives are recorded over the range 4000-400cm^{-1} and the spectral absorptions agreed very well with the earlier studies. The data is presented in TABLE 1 for the sake of comparison along with the results of elemental analysis.

Thermal studies

Thermogravimetric studies are done using the analytical parameters as indicated in the experimental section. The maximum decomposition temperatures (DT_{max}) are presented in TABLE 2. Information about the thermal decomposition of phenothiazine derivatives are rather poor. It is supposed that the thermal degradation in presence of air proceeds due to the oxidation of sulphur atom in the ring to sulphoxide, for the majority of these compounds[25]. The nature of TGA curves indicates that the promazinium and chlorpromazinium picrates degrade in single step, whereas promethazinium and dioxopromethazinium picrates degrade in two and four steps respectively (Figure 1). PP degrades nearly 10% in the first step and 15% in the second step. PMP degrades nearly 28% in the first step. CPP degrades nearly 30% in the first step. In the case of DPP the first, second and third

step degradations are about 10%, 10% and 15% respectively. The major amounts of degradations observed for PMP and CPP are in the first step and for PP and DPP in second and third steps respectively. The weight loss in the fourth step degradation of DPP is very small, to the extent of 3%. The degradation kinetics could not be calculated as the linear degradation portion of the thermogravi metric curve is very small. At 600°C PP has degraded nearly about 67%. At 700°C PMP, CPP and DPP degraded up to 55%, 65% and 67% respectively. The aim of the kinetic study of thermal analysis data is to find the most probable kinetic model which best describes the process and allows the calculation of reliable values for the parameters like, the order of the reaction, activation energy, enthalpy of reaction, entropy of the reaction, Gibb's free energy changes and the frequency factor. Many methods exist to characterize the degradation kinetics of various materials[26-36]. Three methods have been employed Broido's, [32]Coats-Redfern(C-R)[33]and Horowitz-Metzger (H-M) [34] for the evaluation of decomposition kinetics and the results obtained are compared and presented in TABLE 2.

In Broido's method, the thermal degradation pro-

cess is considered to be of first-order and the calculations are done accordingly. In the case of C-R and H-M methods the curve having the highest correlation co-efficient values among the reactions of different orders are considered. The different equations employed to evaluate the degradation kinetics in three

TABLE 1 : The elemental, UV-Visible and FTIR data of PP, PMP, CPP and DPP

Compound	Elemental analysis in % (Theoretical)	UV-Visible absorptions λ_{max} nm (log ε)		FTIR spectral data (In cm^{-1})
PP	C, 53.84(53.69); H, 4.52(4.70); N, 13.78(13.61); S 6.53 (6.23).	248 374	4.16 3.84	3464, 3061,2687,1617, 1542,1460,1364, 1333, 1268,1226, 1172, 762, 745,734,712
PMP	C, 53.43(53.69); H, 4.47(4.70); N, 13.31(13.61); S 6.24(6.23).	250 374	4.18 3.86	3464, 3005, 2709, 1633, 1559, 1466, 1436, 1365, 1158, 1076,787,745,710
DPP	C, 51.83(52.07); H, 4.33 (4.56); N, 13.01(13.20); S, 6.00 (6.04).	223 260 373	4.20 3.74 3.80	3079,2723,1626, 1590,1562, 1470, 1167,1139, 1082, 772,745,708
CPP	C,63.49(63.57); H, 6.57(6.59); N, 8.69(8.73); S 10.01 (9.99).	254 370	3.24 2.88	3434, 3007, 1631, 1339, 1266, 1162, 1130, 1105, 077,966, 848, 790,751,707

TABLE 2 : A comparative, thermogravimetric analytical data of PP, PMP, CPP and DPP using Broido's, Coats-Redfern and Horowitz-Metzger method

|	PP step I	PP step II	PMP step I	CPP step I	DPP step I	DPP step II	DPP step III
Order (n)							
Broido's	1	1	1	1	1	1	1
Coats-Redfern	1.0	0	0	0.25	1	1	1
Horowitz-Metzger	1.0	0.25	0	0	1	1	1
DT$_m$	422	467	511	514	497	506	580
Ea(kjmol^{-1})							
Broido's	102.84	43.98	216.91	168.28	144.08	70.42	17.79
Coats- Redfern	93.53	25.60	148.32	151.73	156.22	63.85	23.62
Horowitz-Metzger	146.47	34.45	158.26	154.42	162.57	69.18	33.28
ΔH(kjmol^{-1})							
Broido' s	99.33	40.10	212.66	164.01	139.95	66.21	12.97
Coats-Redfern	97.04	21.72	144.07	147.46	152.09	59.64	18.80
Horowitz-Metzger	142.96	30.57	154.01	150.15	158.44	64.97	28.46
ΔG(kjmol^{-1})							
Broido's	68.74	143.33	274.26	152.54	154.54	158.50	181.23
Coats- Redfern	129.20	126.10	155.77	138.66	151.21	154.43	157.69
Horowitz-Metzger	166.91	147.45	155.95	152.80	151.30	157.82	186.45
ΔS(J k^{-1} mol^{-1})							
Broido's	-72.49	-221.05	-120.55	-22.32	-29.35	-182.39	-290.11
Coats-Redfern	-76.20	-223.45	-22.90	-17.12	1.78	-187.33	-239.46
Horowitz-Metzger	-56.75	-250.27	-3.80	-5.15	14.37	-183.50	-272.40
A(Sec^{-1})							
Broido's	14.4×10^8	27.7	53.8×10^5	15.7×10^{13}	3.0×10^{11}	31.5×10^2	84.8×10^{-4}
Coats- Redfern	9.2×10^8	20.7	6.8×10^{11}	84.1×10^{12}	12.8×10^{12}	17.3×10^2	37.5×10^{-1}
Horowitz-Metzger	95.6×10^8	82.3×10^{-2}	67.5×10^{11}	19.9×10^{12}	17.9×10^{12}	27.4×10^2	71.4×10^{-3}

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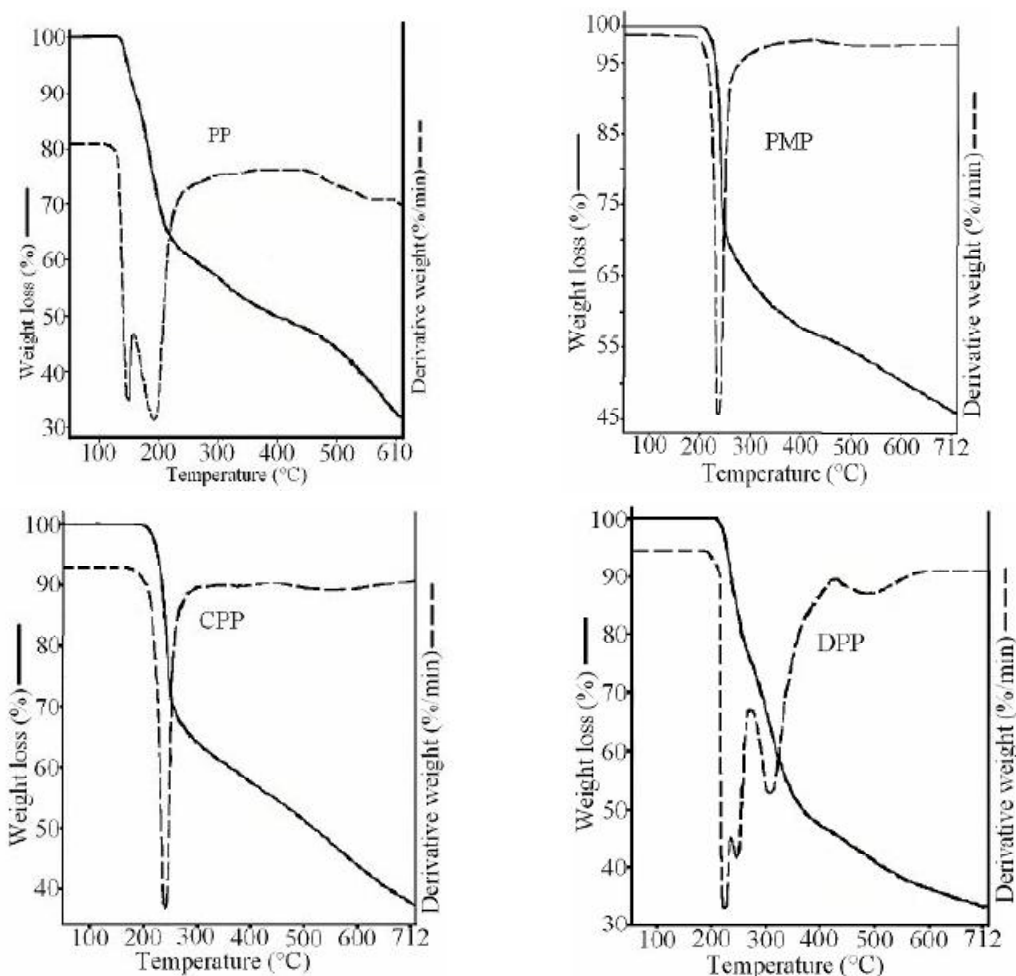
Figure 1: TGA (——) and DTG (——) thermograms of PP, PMP, CPP and DPP

different methods are given below;

Broido's method

$$\ln[-\ln y] = -\frac{E_a}{RT}$$

Coats–Redfern method

$$\ln\left[\frac{-\ln y}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \qquad \text{for n = 1}$$

$$\ln[-\ln y] = \frac{E_a \theta}{R(DT_{max})^2} \qquad \text{for n = 1}$$

Horowitz-Metzger

$$\ln\left[\frac{1 - y^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \qquad \text{for n = 1}$$

$$\ln\left[\frac{1 - y^{1-n}}{(1-n)}\right] = \frac{E_a \theta}{R(DT_{max})^2} \qquad \text{for n = 1}$$

Where, E_a=Activation energy (J/mol), R=Universal gas constant(8.314 J/mol-k),T=Absolute temperature(^{0}K), DT_{max}=Maximum decomposition temperature, A=Arrhenius pre-exponential factor(Sec^{-1}), n=Reaction order, β=Heating rate(^{0}C/min), θ=T-DT_{max} y=(w_t-w∞/ wo- w∞) where wo, w_t and w∞ are the weights of sample before degradation, at time t and after total decomposition respectively.

The graphical plots of $\ln[\ln(1/y)]$ versus 1000/T obtained for PP, PMP, CPP and DPP are presented in figure 2. The value of 'y' presents the compound remaining at temperature T^0K. The slopes of the plots are determined and used to evaluate the activation energies. The values of 'n' reported in the TABLE 2 are the best fit values having the highest correlation coefficient. The activation energy observed are in the order PMP>CPP>DPP>PP. Greater the crystalline nature greater will be the activation energy[35]. The thermodynamic properties like change in enthalpy(ΔH), entropy(ΔS), free energy(ΔG) and frequency factor(A) are calculated using the standard equations as explained elsewhere[36,37] and the values are summarized in TABLE 2. The first order rate constant is determined based on the weight changes with time in the linear degra-
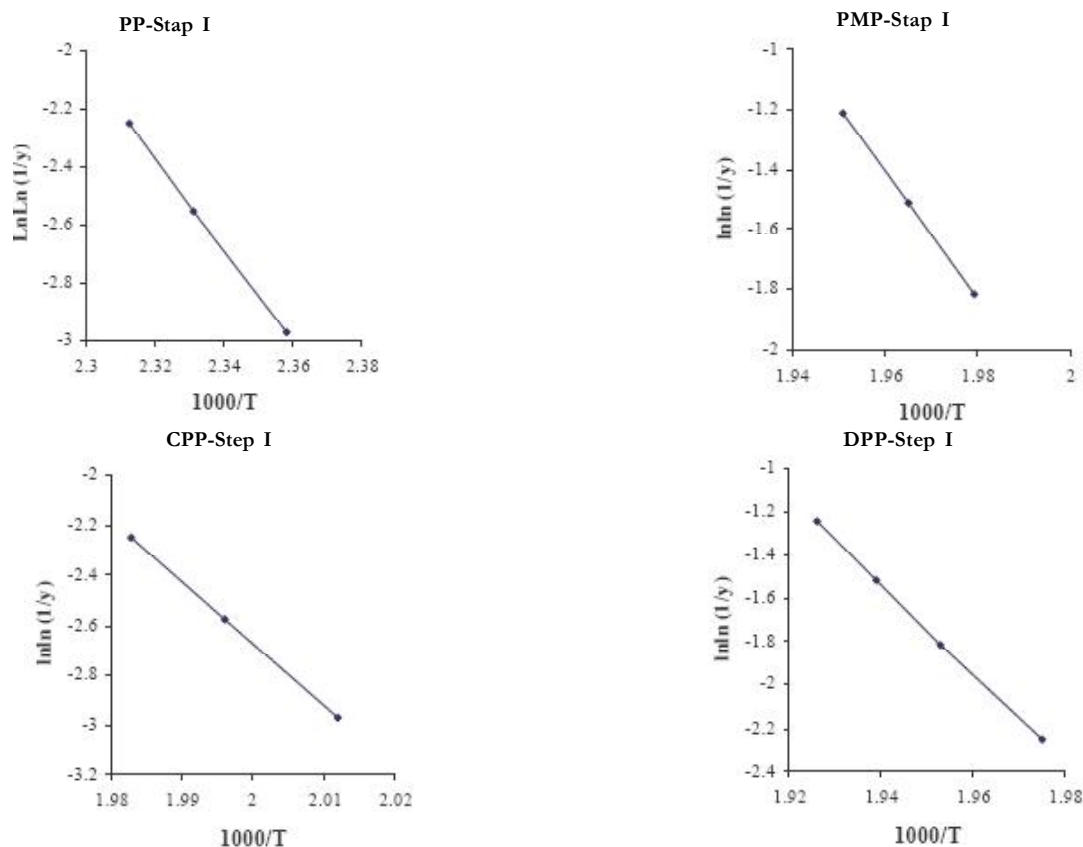
PP-Stap I

PMP-Stap I

CPP-Step I

DPP-Step I

Figure 2 : Graphical plots of ln[ln (1/y)] versus 1000/T of step I of PP, PMP, CPP and DPP

dation portion of the thermogravimetric curve and used for the evaluation of entropy change.

Electrical conductivity

Electrical properties of charge-transfer materials depend largely on different types of packing. Segregated packing usually results in higher conductivities due to the smaller Coulomb barriers between different states of charges on similar molecules. Most of the reported study on electrical properties in literature is based on polycrystalline materials compressed in the form of pellets. The study of solid state electrical conductivity on PP, PMP, CPP and DPP is very important in view of their applications in semiconductor devices[12-13,18-19]. The conductivity measurements are made using the two probe technique as explained in the experimental section on the powdered samples. In order to evaluate the nature of variations of electrical conductivity with temperature, electrical conductivity is measured from ambient to suitable high temperature. The higher temperature limit selected for the electrical conductivity measurements are well within the melting point and decomposition temperatures of the phenothiazinium picrate derivatives as

derived by the TGA curves of the complexes (Figure 1 and TABLE 3). The values of the electrical conductivity are calculated using the equation:

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

Where E=activation energy, k=Boltzman constant, T=Temperature in ^{0}K and σ_0=Constant.

The logarithmic conductivity values were plotted for each phenothiazinium, picrate derivative versus 1000/T. Dependence of electrical conductivity of these complexes with temperature are shown in Figure 3 and the relevant data are summarized in TABLE 3. The observed electrical conductivity values at 30^0C for PP, PMP and CPP are 3.70×10^{-13}, 2.31×10^{-11} and 5.51×10^{-13} Scm^{-1} respectively. The respective earlier room temperature electrical conductivities reported are 6.04×10^{-8}, 1.21×10^{-8}, 6.15×10^{-8} and 4.35×10^{-8} Scm^{-1}. The higher values observed may be due to the presence of impurities. The DPP complex showed conductivity only when the temperature reached 105^0C. The variations of electrical conductivity over the temperature ranges 30-125^{0}C, 30-115^{0}C, 30-130^{0}C and 105-175^{0}C are observed for PP, PMP, CPP and DPP respectively. The plots indicate that these com-

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TABLE 3 : Electrical conductivity data of PP, PMP, CPP and DPP

Compound	Conductivity (σScm^{-1})		E_a (eV)
	At 30^{0}C	At maximum temperature	
PP	3.70×10^{-13}	$2.51 \times 10^{-10}(125^0C)$	0.19 (95-125^{0}C)
PMP	2.31×10^{-11}	$7.0 \times 10^{-8}(115^0C)$	0.17 (30-90^{0}C) 0.79 (95-115^{0}C)
CPP	5.51×10^{-13}	$1.15 \times 10^{-9}(130^0C)$	1.29 (105-130^{0}C)
DPP	2.51×10^{-13} (105^{0}C)	$7.82 \times 10^{-10}(175^0C)$	0.52 (105-145^{0}C) 0.12 (155-175^{0}C)

plexes differ with respect to their ambient and temperature dependent electrical conductivities. It has not been elucidated what rules determine the arrangement of molecules in the solid state, especially the formation of segregated stacks of molecule, though many authors have tried to define these rules[38]. In order to observe higher electrical conductivity there must be an increased contribution of the ionic structure and decrease of intermolecular distance between the charge-transfer molecules along with the decrease in activation energy[39,40]. PP exhibited both metallic and semiconducting behaviors in the temperature range

30-95^{0}C and 95-125^{0}C respectively. All other complexes PMP, CPP and DPP exhibited semiconducting behaviors in the respective temperature ranges studied, figure 3. However, PMP and DPP showed two linear semiconducting ranges. That is 30-90^{0}C as well as 95-115^{0}C and 105-145^{0}C as well as 155-175^{0}C. The activation energies corresponding to the linear variations in the conductivity plots log (conductivity) versus 1000/T are calculated and the data are summarized in TABLE 3. The X-ray diffraction studies are expected to give more information regarding the molecular stacking. Powder X-ray diffraction studies on PP, PMP and CPP have been reported by Leenheer and Heyndrickx[41]. The powder diffraction study on DPP is done for the first time and diffraction data is presented in TABLE 4. The ambient electrical conductivities observed is in the order PMP>CPP>PP> DPP. This indicates that the electrical conductivity is not dependent only on the interplanar stacking but also on other factors like the structure of phenothiazine derivatives and the charge transfer processes. The resultant electrical conductivity observed is due to intermolecular and intramolecular conductivities.
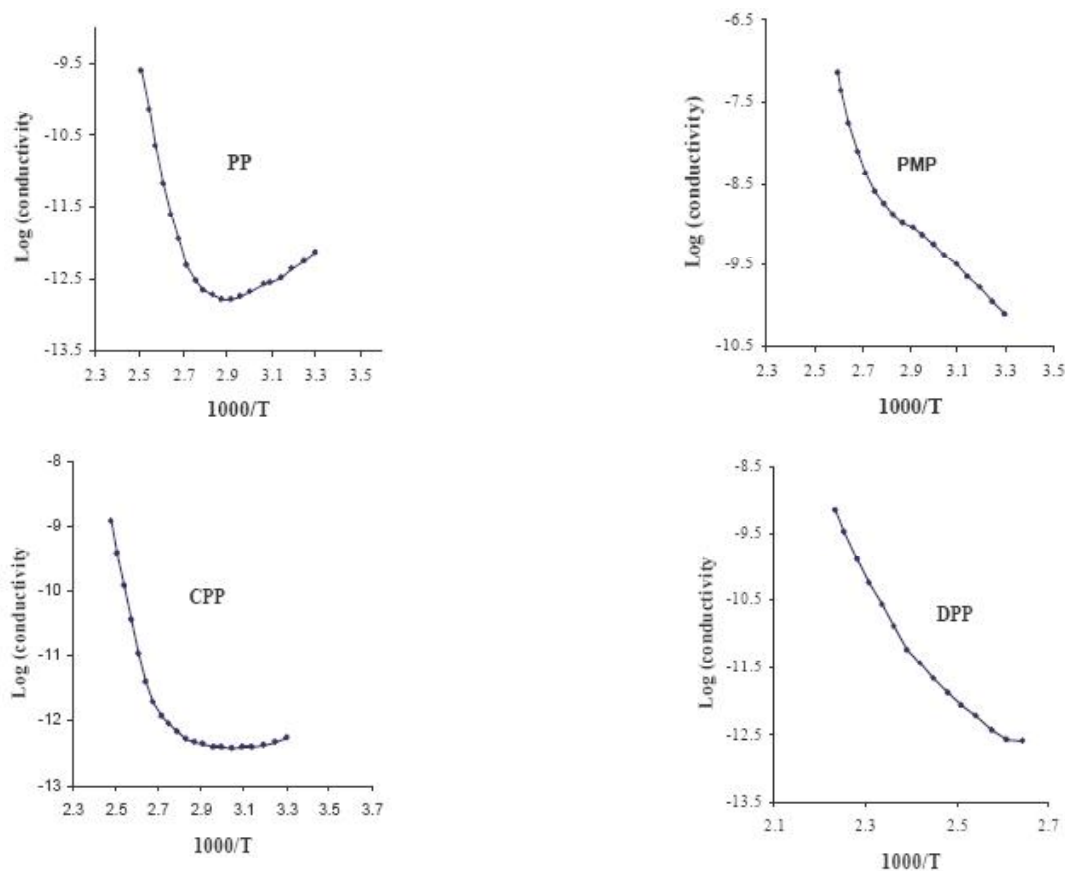

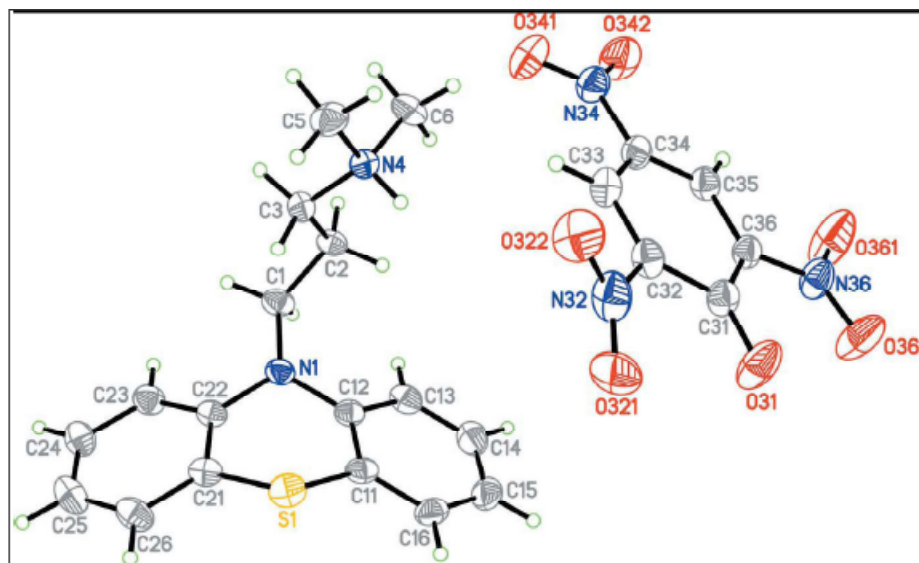**Figure 3 : Electrical conductivity plots of PP, PMP, CPP and DPP**

Figure 4 : ORTEP diagram of promazinium picrate

View of the molecular structure of promazinium picrate, with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms). Only the major orientation of the disordered N32 nitro group is shown.

Hydrogen bonding too has an effect on the activation energy and conduction mechanism[42]. The magnitude of electrical conductivity is greatly affected by the arrangement of molecules in the crystal[43]. Venkatrama Shastri et al. have determined the structure of promethazinium picrate by single crystal X-ray diffraction study[44]. They have stated that promethazinium picrate crystallizes in the triclinic lattice with the space group P1 containing two molecules per unit cell. The picrate group is planar and is almost perpendicular to the promethazine plane. The two groups are joined by hydrogen bond. The crystal structures of PMP and CPP reported elsewhere [23,24]. All the three PP, PMP and CPP complexes crystallize in the triclinic lattice with the space group P 1. DPP is also expected to crystallize in the triclinic lattice with the space group P 1. The ORTEP (Oak Ridge Thermal Ellipsoid Plot) is presented in figures 4-5 and the relevant crystal data are summarized in TABLES 5-6. In all the complexes, the molecular packing is stabilized by N-H.O hydrogen bonds and several C-H.O contacts.

EXPERIMENTAL

Phenothiazine derivatives; Promethazine hydrochloride(May and Baker, India), promazine hydrochloride(Jhon Wyeth, India), dioxo promethazine hydrochloride(VEB, Germany) and chlorpromazine hydrochloride(Smithkline and French, India) were used as received. Picric acid (Qualigens Fine Chemicals, India) was recrystallised twice from doubly distilled water for constant melting point. Elemental analysis for carbon, hydrogen, nitrogen and sulphur were done using Vario EL III CHNS analyzer, Germany. UV-Visible spectra were recorded in alcohol, except in the case of CPP which was recorded in acetonitrile medium using Systronics-117 Spectropho-
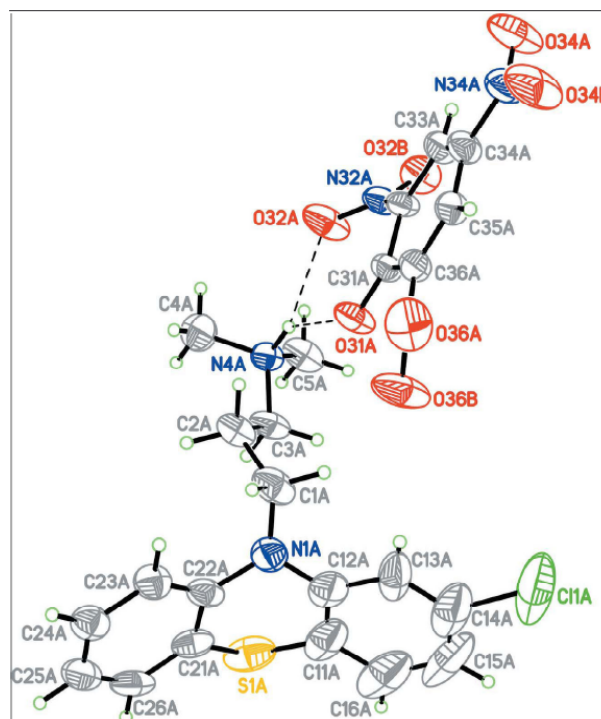

Figure 5 : ORTEP diagram of chlorpromazinium picrate

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TABLE 4 : Powder X-ray diffraction data of DPP

DPP 2θ	d (Å)
8.20	10.77
11.66	7.58
12.32	7.18
14.29	6.19
15.72	5.63
16.27	5.44
16.47	5.38
18.51	4.79
19.48	4.55
20.04	4.43
20.33	4.36
22.0	4.04
23.04	3.86
23.49	3.78
23.60	3.75
24.40	3.64
24.79	3.59
25.82	3.45
26.86	3.32
27.08	3.29
28.40	3.14
29.35	3.04
29.81	2.99

TABLE 5 : Crystal data and structure refinement for promazinium picrate

Empirical formula	$C_{23} H_{23} N_5 O_7 S$	
Formula weight	513.52	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a=10.0611(6)Å	α=85.649(6)^0
	b=10.2518(7)Å	β=78.414(5)^0
	c=11.9841(8)Å	γ=82.040(5)^0
Volume	1197.77(13) Å^3	
Z	2	
Final R indices[I>2sigma(I)]	R1=0.0461, wR2= 0.1249	

tometer Ahmedabad, India, with 1.0cm quartz cells. The I R spectra were taken using JASCO FTIR-460 PLUS spectrophotometer Japan. Stoe IPDSII two-circle diffractometer was used to measure the reflections. SHELX 97 was used to refine single crystal data. SHELXTL- plus software was used to prepare material for publication. A Rigaku Miniflux X-ray diffractometer; model IGC2, Rigaku Denki Co Ltd. Jpn. Source: 1.5405 Å λ was used to study the powder XRD of the samples. For conductivity measurements, all the samples were compressed into pellets

TABLE 6 : Crystal data and structure refinement for chlorpromazinium picrate

Empirical formula	$C_{23} H_{22} Cl$	$N_5 O_7 S$
Formula weight	547.97	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P	1
Unit cell dimensions	a=12.3355(14)Å	α=108.758(10)^0
	b=14.6631(19)Å	β=104.675(10)^0
	c=15.5340(19)Å	γ=100.922(9)^0
Volume	2458.5(5)Å^3	
Z	4	
Final R indices[I>2sigma(I)]	R1=0.0949,wR2=0.2352	

of 1.30cm diameter and thickness ranging around 0.1-0.2cm using Perkin-Elmer KBr die under a pressure of 250kg/cm². The TSI Techno search instruments, Thane, India, KBr press model-15 ton capacity was used for applying pressure. Conducting silver paint was coated on both flat surfaces of the pellets and electrical contacts with the electrodes were made by using the same paint. The resistance measurements were done using DOT-402 Digital Milli Ohm Meter and DOT-425 Insulation resistance tester, Bhandari Electronics and electricals, Bangalore, India. Thermogravimetric analysis of all the complexes except PP were performed in air atmosphere using TGA-7 Analyzer, Perkin-Elmer, USA, from ambient temperature to 700⁰C at the heating rate of 10⁰C /min and with an air flow of 100mL/min. In the case of PP the sample was heated up to 600⁰C. The charge-transfer complexes were prepared, in general, by taking appropriate amounts of the components for 1:1 stiochemetry in doubly distilled water and mixing them. All the derivatives formed C-T complexes with picric acid instantaneously at room temperature. The separated C-T complexes in each case was filtered using G4 glass crucible and washed thoroughly with doubly distilled water and dried in vacuum desiccator over phosphorous pentoxide. PP, PMP, CPP and DPP were greenish yellow, brick red, orange and bright yellow in colour respectively. All the complexes were water insoluble.

CONCLUSION

The values of electrical conductivity showed variations between 10^{-13}-10^{-8} with temperature for the C-T complexes studied. Out of these complexes PMP showed ~100 times higher electrical conductivity

compared to the other three complexes. The S=O groups at position 5, Cl group at position 2 and branching in substitution 10 seem to decrease the intermolecular conductivity. From the data it is clear that the charge-transfer processes are neither very strong nor very week. All the complexes are thermally stable upto 100^0C. The temperature range in which these phenothiazinium picrates exhibit semi-conducting behaviors can be explored for the fabrication of suitable electronic devices.

ACKNOWLEDGEMENT

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