Some Physico-Chemical Studies on Molecular Semiconductors Based on Charge Transfer Complexes of Substituted Phenothiazines with Iodine

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The synthesis, chemical and structural characterizations, and thermal, spectral, electrical, and magnetic properties of six molecular semiconductors based on the charge transfer complexes of substituted phenothiazines namely; phenothiazine, 2-chlorophenothiazine, 2-(trifluoromethyl)phenothiazine, 2-acetylphenothiazine, *N*-acetylphenothiazine, and *N*-benzoylphenothiazine with molecular iodine have been reported in this paper. These complexes have been found to have 2 : 3 stoichiometries. X-Ray diffraction data show that first three complexes have orthorhombic structure whereas the other three are amorphous. Thermal analysis shows that the complexes are thermally stable upto 120 °C. The existence of monomeric and dimeric cationic species of phenothiazines has been proposed on the basis of spectral data. These complexes have been found to be molecular semiconductors having moderately high electrical conductivities and activation energies. The segregated stacking of phenothiazine and iodine moieties has been proposed to be responsible for high conductivity values and a mixed conductivity mechanism accounts for temperature dependence of electrical conductivities of these complexes.

Molecular materials with remarkable physical properties have been extensively studied in the past two decades.[1–3] Potentialities offered by these materials have been tremendous in the development of molecular level electronic devices as is evident from the number of patented compounds based on organic charge transfer solids. The observation of semiconductivity in this class of materials has opened an era of developing and testing these materials for a number of technological applications. The discoveries of organic metals and organic superconductors have resulted in an interdisciplinary approach involving synthetic and physical chemists, solid state physicists, and material scientists. This upsurge of activity has its genesis in the discovery of high electrical conductivities of bromine complex of perylenes by H. Akamatu et al.[4] However, the iodine complexes with various types of electron donors have played the key role in the development of organic electronic materials, mainly because iodine is such an acceptor, which forms charge-transfer complexes from the weakest to the strongest with various electron donors.[5] The charge-transfer complexes of iodine with phenothiazines which are fairly strong donors, were reported first by Y. Matsunaga.[6,7] This complex was found to be an organic semiconductor. The ratio of donor to the acceptor was found to be 2 : 3 and it had a fairly high electrical conductivity. The electrical resistivity of the complex was dependent on its composition, 2 : 3 being the minimum resistivity composition. Similar compositional dependence of electrical and magnetic properties of some related phenothiazine–iodine complexes were reported by Matsunaga and other workers.[8–11] A complex cation radical of phenothiazine was proposed to be responsible for high conductivity of this class of compounds in which electronic conduction takes place between phenothiazines in different oxidation states. Iida[12] proposed that the X-ray diffraction studies on phenothiazine cation radical salts will help us in determining their structure and arrangement of stacking in solid state. In a study of thermoelectric power of iodine complexes of aromatic diamines and thiazines, Akamatu et al.[13,14] reported the hole conduction for phenothiazine–iodine complexes whereas *N*-methylphenothiazine–iodine complex had temperature dependent mixed conductivity mechanism, hole conduction in higher temperature region and electron conduction in the lower temperature region. The interest in the phenothiazine–iodine complexes continued and Resonance Raman and ^{129}I Mössbauer spectroscopic study of this complex was reported very recently by Sakai et al.[15] It was shown that two iodine species in this complex were present consisting of a distorted I_3^- unit and I_2 unit strongly coordinated with this I_3^- unit in which about three electrons for five phenothiazine molecules are transferred to the iodine which are delocalized on the thirteen iodine atoms. Though the single crystal of this compound has not yet been grown, the powder X-ray diffraction may yield some information about the crystal structure of this or related complexes. Electrochemical oxidation of phenothiazine in presence of different inorganic ions yielded stoichiometric complex salts of phenothiazines having 1 : 1, 3 : 2, and 2 : 1 compositions.[16]

The literature survey reveals that the interest in phenothiazine–iodine complexes had mainly focussed around the parent compound and some of structurally related analogues. A few complexes of ring substituted and N-substituted phenothiazines with iodine have been reported.[8,10] However, still a large number of complexes of substituted phenothiazines with iodine have not been synthesized and studied. It is, therefore, pertinent to study the role of electronic and structural modifications on the solid state properties of these complexes. We report herein six new complexes of substituted phenothiazines with iodine on which detailed X-ray diffraction, photoacoustic, electronic, and reflectance, infrared and nuclear magnetic resonance spectral studies have been performed. Electrical, magnetic, and thermal studies have also been undertaken.

Experimental

Materials and Methods. Phenothiazine (PTZ), 2-chlorophenothiazine (CPZ), 2-(trifluoromethyl)phenothiazine (TPZ), and 2-acetylphenothiazine (APZ) were commercially obtained from Aldrich Chemie (F.R.G.). Further purifications were done by vacuum sublimation and fractional crystallization using cyclohexane–chloroform–ethanol mixture. Iodine obtained from E. Merck was further purified by vacuum sublimation. *N*-Acetylphenothiazine (NAPZ) was prepared by acetylation of phenothiazine with acetic anhydride according to the literature procedure.17) The product obtained was recrystallized from ethanol. *N*-benzoylphenothiazine (NBPZ) was prepared by the reaction of phenothiazine with benzoyl chloride in a sealed tube at 100—110 °C as reported in the literature17) and purified by recrystallization in ethanol. The purities of the compounds were checked from their melting points, elemental analyses, electronic, infrared, and NMR spectral data which were found to agree well with the literature values.

In general, the charge-transfer complexes of these phenothiazines with iodine were prepared by taking appropriate amounts of the components for 2 : 3 stoichiometry in suitable solvents and by mixing their dilute solutions. The dark brown colored crystalline complexes separated out when these solutions were kept for about two weeks. The resulting precipitates were collected by filtration washed three times with solvents and dried over anhydrous calcium chloride. The detailed procedures, yields, melting points, and elemental analyses for different complexes are given below:

$(PTZ)_2$-$(I_2)_3$: A dilute solution of PTZ (0.800 g, 40 mmol) in ether (50 mL) was slowly added to the dilute solution of I_2 (1.550 g, 60 mmol) in ether (50 mL). Yield: 90%, mp 175—178 °C. Elemental analysis; Found: C, 24.60; H, 1.98; N, 2.38; S, 5.34%. Calcd for $C_{24}H_{18}I_6N_2S_2$: C, 24.83; H, 1.55; N, 2.41; S, 5.52%.

$(CPZ)_2$-$(I_2)_3$: A dilute solution of CPZ (0.940 g, 40 mmol) in ether (50 mL) was slowly added to the dilute solution of I_2 (1.550 g, 60 mmol) in ether (50 mL). Yield: 91%, mp 125—128 °C. Elemental analysis; Found: C, 23.18; H, 1.77; Cl, 5.47; N, 2.12; S, 5.01%. Calcd for $C_{24}H_{16}Cl_2I_6N_2S_2$: C, 23.44; H, 1.30; Cl, 5.78; N, 2.28; S, 5.21%.

$(APZ)_2$-$(I_2)_3$: A dilute solution of APZ (0.970 g, 40 mmol) in ether (50 mL) was slowly added to the dilute solution of I_2 (1.550 g, 60 mmol) in ether (50 mL). Yield: 92%, mp 155—158 °C. Elemental analysis; Found: C, 26.79; H, 1.92; N, 2.69; S, 5.01%. Calcd for $C_{28}H_{22}I_6N_2O_2S_2$: C, 27.02; H, 1.77; N, 2.25; S, 5.15%.

$(TPZ)_2$-$(I_2)_3$: A dilute solution of TPZ (1.100 g, 40 mmol) in ether (50 mL) was slowly added to the dilute solution of I_2 (1.550 g, 60 mmol) in ether (50 mL). Yield: 90%, mp 115—118 °C. Elemental analysis; Found: C, 23.93; H, 1.29; N, 2.66; S, 4.69%. Calcd for $C_{26}H_{16}F_6I_6N_2S_2$: C, 24.08; H, 1.23; N, 2.16; S, 4.94%.

$(NAPZ)_2$-$(I_2)_3$: A dilute solution of NAPZ (0.970 g, 40 mmol) in ether (50 mL) was slowly added to the dilute solution of I_2 (1.550 g, 60 mmol) in ether (50 mL). Yield: 92%, mp more than 320 °C. Elemental analysis; Found: C, 27.31; H, 1.68; N, 2.34; S, 4.95%. Calcd for $C_{28}H_{22}I_6N_2O_2S_2$: C, 27.02; H, 1.77; N, 2.25; S, 5.15%.

$(NBPZ)_2$-$(I_2)_3$: A dilute solution of NBPZ (1.350 g, 40 mmol) in ether (50 mL) was slowly added to the dilute solution of I_2 (1.550 g, 60 mmol) in ether (50 mL). Yield: 89%, mp 190—193 °C. Elemental analysis; Found: C, 33.60; H, 1.92; N, 2.80; S, 4.38%. Calcd for $C_{38}H_{26}I_6N_2O_2S_2$: C, 33.35; H, 1.90; N, 2.05; S, 4.68%.

Measurements. All the complexes have been obtained as powdered or polycrystalline solids and attempts to grow single crystals failed. Therefore, only powder X-ray diffraction data could be obtained. The X-ray diffraction patterns were recorded on Philips X-ray diffractometer PW 1710 using Cu *Kα* radiation. The electronic absorption spectra were recorded on Cary 2390 and Shimadzu UV-160A spectrophotometers. Reflectance spectra were recorded on Cary 2390 spectrophotometer. Infrared absorption spectra were recorded on Perkin-Elmer 783 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL FX-90 Q FT-NMR spectrometer. Electrical measurements were made on Wayne Kerr Automatic Precision Bridge B905. For electrical measurements, the pellets were prepared at a pressure ca. 15 kbar and measurements were repeated at least twice to get reproducible values of various physical properties. AC conductivities of the samples were measured at two different frequencies 1 kHz and 10 kHz at different temperatures in the range (293—403 K). The magnetic measurements were made on a Cahn–Faraday balance at 10 K gauss magnetic field. Photoacoustic spectral measurements were made on a single beam photoacoustic spectrometer designed and fabricated in the spectroscopy section, Department of Physics, B.H.U., Varanasi. Thermogravimetric analyses were done on Stanton Red Croft STA-780 series Unit. The analytical constants were: heating rate: 5 to 10 °C min^{-1}; chart speed: 1000 mm h^{-1}; reference: Al_2O_3; thermocouple: Platinum–Rhodium. The analysis was made in the atmosphere of air between room temperature and 700 °C.

Results and Discussion

Stoichiometries of the Complexes: A Thermogravimetric Analysis. All of the phenothiazine–iodine complexes reported in this paper have been obtained as dark colored solids. When these complexes are heated on a spatula over hot plate, vigorous liberation of iodine results. Thermogravimetric analyses of these complexes show two stage decompositions. A representative thermogravimetric and differential thermogravimetric curve for phenothiazine–iodine complex has been shown in Fig. 1. The phenothiazine–iodine complex shows no weight loss upto 100 °C indicating that the air-dry compound contained no residual humidity. Between 145—290 °C, the labile molecular iodine is lost, the rate of decomposition being maximum at 170 °C as indicated by its DTG curve. DTA curve indicates an exothermic peak at 170 °C. Later, all the residual material is lost between 290—700 °C. Similar curves were obtained for other complexes as well. This data led us to calculate the stoichiometry of the complexes and their decomposition characteristics. Since elemental analyses show 2 : 3 stoichiometries of the complexes, the relative molecular mass of the complex was calcu-

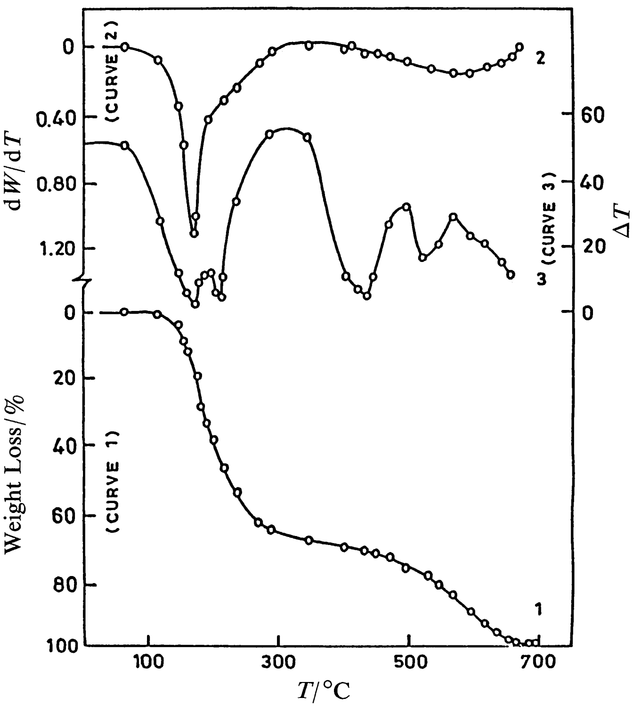

Fig. 1. Thermogravimetric (1), differential thermogravimetric (2), and differential thermal analysis (3) curves for phenothiazine–iodine complex.

lated on this basis. The decomposition steps are as follows:

$$(PTZ)_2(I_2)_3 \longrightarrow 2PTZ + 3I_2 \uparrow \qquad (I)$$

$$2PTZ \longrightarrow 2(PTZ) \uparrow \qquad (II)$$

Though 2:3 stoichiometries of the phenothiazine–iodine complexes have been shown to be most stable and having highest electrical conductivities, there has been a lot of controversy about the stoichiometries of this class of molecular semiconductors. Matsunaga et al.[18] proposed the structure of the complex as $(PTZ)_2{}^+I_5{}^- \cdot 1/2I_2$ in which $1/2\ I_2$ is expected to be more loosely bound than those in pentaiodide. If this is so, it should result in about 10.94% loss of molecular iodine in the first stage of thermal decomposition. However, we do not observe any decomposition step corresponding to this weight loss. Similarly 2:5.2 composition proposed on the basis of Resonance Raman and Mössbauer studies can also be ruled out on the basis of thermogravimetric analysis. Thus, the phenothiazine–iodine complexes have 2:3 stoichiometries and are thermally stable upto 120 °C.

The dissociation of phenothiazine–iodine complexes in organic solvents further supports above observations. In carbon tetrachloride these complexes show intense violet color indicating the presence of molecular iodine, similar to the tetramethylammonium pentaiodides.[19] In relatively polar solvents like acetonitrile, solubility of the complexes increases indicating dative nature of these complexes. These species have been identified on the basis of their spectral data.

Spectral Data. The electronic absorption spectra of the complexes dispersed in Nujol have bands at 14.5, 20.0, 21.1, 26.7, and 30.8×10^3 cm^{-1}. The diffuse reflectance spectra showed bands at 15.1, 15.6, and 20.5×10^3 cm^{-1}. The photoacoustic spectra of solid complexes indicated bands at 12.8, 14.7, 15.6, and 18.9×10^3 cm^{-1}. The solution spectra in carbon tetrachloride and chloroform showed bands at 12.6, 19.4, 28.2, and 32.3×10^3 cm^{-1} and 11.9, 15.8, 19.7, and 33.5×10^3 cm^{-1}, respectively. Whereas in polar solvents like acetonitrile and methanol, bands at 15.5, 20.0, 21.6, 24.0, and 28.2 (sh)$\times10^3$ cm^{-1} were found. Aged solutions of the complexes in acetonitrile having lush green colors were found to have bands at 11.4, 15.2, 19.3, 24.0, and 34.5×10^3 cm^{-1}. The 11.4×10^3 cm^{-1} band on dilution by solvent, shifted to 11.9×10^3 cm^{-1}. These spectral data indicate that the phenothiazine–iodine complexes have a number of molecular species of phenothiazines in solution, which may possibly be present in solid state as well on the basis of their electronic spectra. The intense violet color of the complexes kept in nonpolar solvents having bands at 19.4×10^3 cm^{-1} indicates the presence of molecular iodine, which in polar solvents gets complexed and thus blue shifted to 21.6 and 24.0×10^3 cm^{-1}. The solvent assisted dimerization of phenothiazine cation radicals, as proposed by Foster et al.,[20] may possibly be true nature of molecular species present in polar solvents. Similar results have been obtained for DDQ complexes.[21]

The above observations are further supported from the vibrational spectra of the complexes which are identical with those reported by Matsunaga et al.[18] The sharp N–H peaks of phenothiazines between 3320—3380 cm^{-1} are replaced by broad bands in this region in the complex indicating the existence of weakly acidic N–H in the cation radical of phenothiazine, but the bands at 1560, 1590, 1050, 930, 890, and 780 cm^{-1} indicate the existence of some neutral phenothiazines in solid state. Thus, these complexes are expected to have mixed valence structures, which help in electronic conduction.

The ^{1}H NMR spectra of phenothiazines in $CDCl_3$ at room temperature shows two peaks at δ=1.55 and 5.84 ppm vs. TMS exchangeable with D_2O. These peaks have been attributed to two conformations of N–H protons; 'H-intra' (75%) δ=5.84, 'H-extra' (25%) δ=1.55 as reported.[22] The ^{1}H NMR spectra of complexes in $CDCl_3$ give exchangeable protons at δ=1.57 and 10.20. The former confirms the existence of 'H-extra' conformation as such in zero oxidation state while the later confirms the existence of acidic N–H protons. Therefore, the NMR spectra of the complexes in solution indicate the existence of mixed valence structures possibly present in solid state. The X-ray diffraction data for these complexes have been given below:

X-Ray Diffraction Data. The powder X-ray diffraction data of three complexes were indexed by Ito's method.[23] The observation of diffraction patterns in the present set of complexes rules out the possibility of any interference by heavy halogen contents in the complexes. The lattice constants of the complexes are as follows:

(i) $(\mathrm{PTZ})_2$–$(\mathrm{I}_2)_3$: *a* 4.87 Å, *b* 9.18 Å, *c* 18.51 Å.
(ii) $(\mathrm{CPZ})_2$–$(\mathrm{I}_2)_3$: *a* 6.90 Å, *b* 9.07 Å, *c* 19.56 Å.
(iii) $(\mathrm{TPZ})_2$–$(\mathrm{I}_2)_3$: *a* 6.93 Å, *b* 9.52 Å, *c* 24.64 Å.

The indexing of the data showed that all the phenothiazine–iodine complexes have orthorhombic crystal structures as for the parent compounds with almost similar lattice parameters.[24] Similar results have been obtained for PTZ–DDQ complexes.[25] *N*-Methylphenothiazine–iodine complex has been reported to have the orthorhombic crystal structures with lattice constants as *a* 11.4 Å, *b* 21.4 Å, *c* 21.1 Å.[11] Our values of *a*, *b*, and *c* are quite different from the above but they all have the same crystal structure. No data on crystal structure of any other complex of iodine with phenothiazines is available for comparison. The lattice constants of the parent compounds and the iodine complexes being comparable indicate that the unit cells of the complexes contain arrays of phenothiazine species in which pentaiodides occupy vacant lattice sites as speculated by Sakai et al.[15] Face to face stacking of folded phenothiazine cation radicals resulting in linear extended chain as proposed by Iida[12] may possibly be structure of high conductivity complexes.

Electrical and Magnetic Data: The electrical properties of iodine complexes of phenothiazines have been extensively studied.[26] However, the electrical conductivities of the iodine complexes of present set of substituted phenothiazines have not yet been reported. Both N-substitution and ring substitution with both electron withdrawing and electron donating group has been studied to learn about the electronic, structural, and conformational aspects of these complexes.

The logarithms of the conductivities of the complexes, plotted against the reciprocal temperatures have been shown in Figs. 2—4. The plots were nonlinear showing marked decrease at higher temperatures than at lower temperatures. Bandrauk et al.[26] proposed that the deviation from linearity was indicative of changes in conductivity mechanisms. The electrical and magnetic data of the complexes have been presented in Table 1.

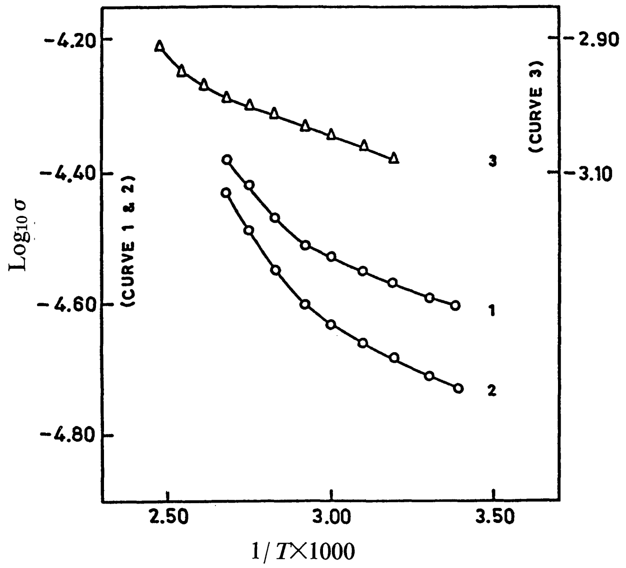

Fig. 3. The plot of logarithm of conductivities vs. T^{-1} for complexes of (1) 2-chlorophenothiazine–iodine at 10 kHz, (2) 2-chlorophenothiazine–iodine at 1 kHz, and (3) 2-acetylphenothiazine–iodine at 10 kHz.

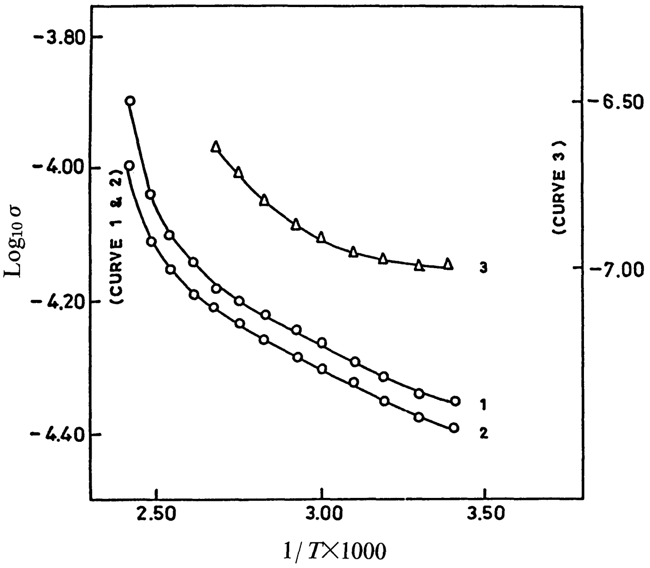

Fig. 2. The plot of logarithm of conductivities vs. T^{-1} for complexes of (1) phenothiazine–iodine at 10 kHz, (2) phenothiazine–iodine at 1 kHz, and (3) 2-(trifluoromethyl)phenothiazine–iodine at 10 kHz.

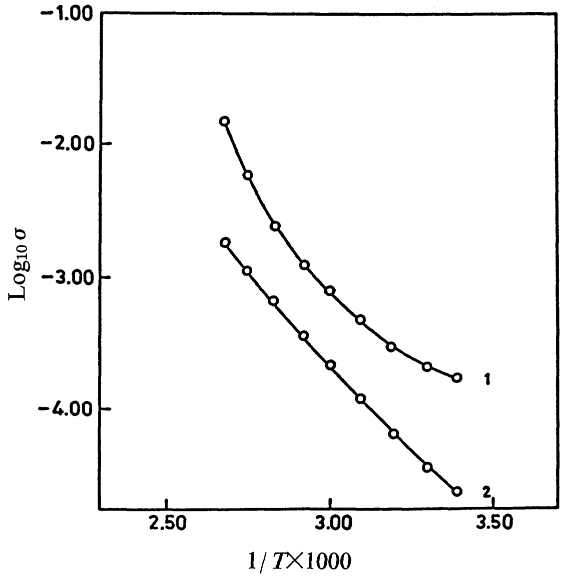

Fig. 4. The plot of logarithm of conductivities vs. T^{-1} for complexes of (1) *N*-acetylphenothiazine–iodine at 10 kHz and (2) *N*-benzoylphenothiazine–iodine at 10 kHz.

Table 1. Electrical and Magnetic Properties of Charge-Transfer Complexes of Iodine with Some Substituted Phenothiazines

Compounds	Electrical conductivity at r.t./μS cm^{-1}			Energy of activation for electrical conductivity (eV) at frequency 10 kHz		Corrected magnetic susceptibility	Magnetic moment
	10 kHz	1 kHz	100 Hz	E_{a_1}	E_{a_2}	(ml mol^{-1})×10^{-6}	BM
$(PTZ)_2$–$(I_2)_3$	44.67	40.74	—	0.15	0.04	3626.16	2.93
$(CPZ)_2$–$(I_2)_3$	24.98	18.71	15.92	0.12	0.04	3394.83	2.83
$(APZ)_2$–$(I_2)_3$	336.00	—	—	0.06	0.07	1338.73	1.78
$(TPZ)_2$–$(I_2)_3$	0.10	0.03	—	0.20	0.06	3422.41	2.84
$(NAPZ)_2$–$(I_2)_3$	174.98	144.37	127.40	0.99	0.20	—	Diamagnetic
$(NBPZ)_2$–$(I_2)_3$	24.25	19.88	17.55	0.44	—	—	Diamagnetic

Room temperate electrical conductivities of the complexes vary in the order;

$$(APZ)_2\text{–}(I_2)_3 > (NAPZ)_2\text{–}(I_2)_3 > (PTZ)_2\text{–}(I_2)_3 > (CPZ)_2\text{–}(I_2)_3 \approx (NBPZ)_2\text{–}(I_2)_3 > (TPZ)_2\text{–}(I_2)_3.$$

These values are much lower than reported for other phenothiazine–iodine complexes. This may be due to different structural factors, such as the size of crystallites, amorphous nature of some of them, and the changes due to different functional groups. The energy of activation determined from the slopes of two linear portions have also been presented in Table 1, they have been labelled as E_{a_1} and E_{a_2}. E_{a_1} has been found to be higher than E_{a_2} but both the values are characteristic of organic semiconductors. These values have been found to vary in order;

$$(NAPZ)_2\text{–}(I_2)_3 > (NBPZ)_2\text{–}(I_2)_3 > (TPZ)_2\text{–}(I_2)_3 > (PTZ)_2\text{–}(I_2)_3 > (CPZ)_2\text{–}(I_2)_3 > (APZ)_2\text{–}(I_2)_3.$$

It has been well established that the charge-transfer interaction between the ion radicals leads to a marked decrease paramagnetic susceptibilities of ion radical salts.[12] Magnetic susceptibilities and magnetic moments of the charge-transfer salts of iodine with substituted phenothiazines at room temperatures have been determined and given in Table 1. The small rise in weight of the samples of $(PTZ)_2$–$(I_2)_3$, $(CPZ)_2$–$(I_2)_3$, $(APZ)_2$–$(I_2)_3$, $(TPZ)_2$–$(I_2)_3$ on application of magnetic field of strength 10 K gauss shows that these compounds are weakly paramagnetic. The corrected molar magnetic susceptibilities yield magnetic moments of the order of about 1.78, 2.83, and 2.93 BM respectively, indicating the presence of some unpaired spins in the complexes, either on molecular or impurity sites of these partially ionized solids. $(NAPZ)_2$–$(I_2)_3$ and $(NBPZ)_2$–$(I_2)_3$ show no change in weight on application of magnetic field, therefore these compounds are diamagnetic possibly due to strong antiferromagnetic interactions.

Summary

The phenothiazine–iodine complexes reported in this paper have been found as molecular semiconductors having quite different physical properties. This highlights the importance of both electronic and structural factors on which physical properties of this class of complexes depend. Segregated stacking and mixed conductivity mechanisms have been proposed to account for electrical properties of these complexes.

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