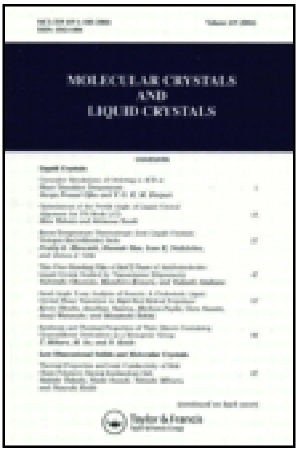

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Molecular Semiconductors Based on Charge Transfer Complexes of Some Substituted Phenothiazines with Tetracyanoethylene

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Molecular Semiconductors Based on Charge Transfer Complexes of Some Substituted Phenothiazines with Tetracyanoethylene

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Molecular semiconductors based on charge transfer complexes of tetracyanoethylene (TCNE) with phenothiazines namely phenothiazine, 2-chlorophenothiazine, 2-acetylphenothiazine and 2-(trifluoro)methylphenothiazine have been prepared and characterized by elemental analysis, thermal, spectral and X-ray diffraction methods. The thermal decomposition behavior of these materials indicates that they are thermally stable up to about 100°C and then proceed to stoichiometric (1:1) weight losses corresponding to TCNE and phenothiazines. The stoichiometries were confirmed further from the combustion data. The existence of radical cations of phenothiazines and radical anions of TCNE were confirmed from their electronic and infrared spectral data. The preferential complexation with H-intra form of phenothiazines were indicated by their ^{1}H NMR spectra. These materials were polycrystalline in nature and the powder X-ray diffraction data give their structures to be orthorhombic. The electrical conductivities are rather low but they obey the characteristic molecular semiconductor behavior with two activation energies indicating mixed conduction behavior. The magnetic measurements indicate that these materials are diamagnetic in nature.

Keywords: molecular semiconductor; charge transfer complex; stoichiometry; donors; acceptor; powder X-ray diffraction; AC conductivity; magnetic susceptibility; thermal stability

INTRODUCTION

We have been pursuing a research program aimed at the preparation and characterization of molecular electronic materials based on charge transfer complexes.[1–4] In this paper, we report a detailed study of thermal, structural, spectral, electrical and magnetic properties of some molecular semiconductors based on tetracyanoethylene (TCNE) as electron acceptor and phenothiazine, 2-chlorophenothiazine, 2-acetylphenothiazine and 2-(CF_3)-phenothiazine as electron donors. The choice of donors and acceptors were based on their electron accepting and donating properties, which are moderately high. Although some charge transfer complexes of TCNE have been studied for their electrical properties but neither these com-

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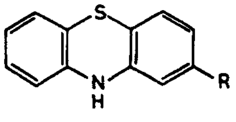
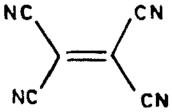
binations have been studied nor a detailed study has been undertaken on this class of molecular materials.[5-7] TCNE has yielded a number of ferromagnetic molecular charge transfer complexes with ferrocenes.[8] The existence of molecular anion of TCNE has been proved on the basis of spectral and magnetic measurements. The ferrocenium-TCNE salt exhibits ferromagnetic behavior above 60 K but it displays the onset of spontaneous magnetization in zero applied field below 5 K consistent with a three dimensional ferromagnetic state.[9] The solid state structure of this salt contains alternating cations and anions. The crystal and molecular structure of the charge transfer salt of decamethylcobaltacene and TCNE having 2:1 stoichiometry have been reported.[10] The electronic structure and spectra of TCNE, $TCNE^{1-}$ and $TCNE^{2-}$ have been studied. These systems have led to an understanding of the microscopic basis for the cooperative magnetic phenomena in molecular materials.

Since phenothiazines are relatively strong donors, the possibility of formation of their ionic radical salts with TCNE exists. In this paper, the synthesis and physicochemical characterization of some charge transfer complexes of substituted phenothiazines with TCNE have been reported. In particular, the complexes of phenothiazine (I), 2-chlorophenothiazine (II), 2-acetylphenothiazine (III) and 2-(trifluoro)methylphenothiazine (IV) with TCNE (V) have been prepared and their spectral, thermal, structural, electrical and magnetic properties have been studied. The molecular structures of electron donors and acceptor are given below with appropriate numbering.



(I - IV)



(V)

where (I) R = H; (II) R = —Cl; (III) R = —$COCH_3$ and (IV) R = —CF_3.

EXPERIMENTAL

Materials and Methods

All of the compounds (I–V) were obtained from Aldrich. They were further purified by vacuum sublimation and fractional crystallization from cyclohexane-chloroform-ethanol mixtures. Their purities were checked by their melting points, elemental analyses and spectral data, which agree quite well with the literature values.

The charge transfer complexes of these phenothiazines with TCNE were prepared, in general, by taking appropriate amounts of the components for 1:1 stoichiometry in suitable solvents and mixing them. The deep dark colored complexes separated, when these solutions were kept overnight. The resulting precipitates were collected by filtration, washed twice with solvent and dried under reduced pressure over anhydrous calcium chloride. The detailed procedures, yields, melting points and elemental analyses for different complexes are given below:

Phenothiazine-tetracyanoethylene complex (I–V). A solution of I (0.400 g, 20 mmol) in ether (25 mL) was slowly added to the solution of V (0.260 g, 20 mmol) in ether (25 mL). Yield 85%, m.p. 115–120°C.
Elemental analysis; Found: C 65.76, H 2.82, N 21.43, S 9.59%
Calculated for $C_{18}H_9N_5S$: C 65.98, H 2.74, N 21.38, S 9.77%

2-Chlorophenothiazine-tetracyanoethylene complex (II–V). A solution of II (0.470 g, 20 mmol) in ether (25 mL) was slowly added to the solution of V (0.260 g, 20 mmol) in ether (25 mL). Yield 80%, m.p. 130–135°C.
Elemental analysis; Found: C 59.69, H 2.62, Cl 9.58, N 19.23, S 8.65%
Calculated for $C_{18}H_8N_5SCl$: C 59.73, H 2.21, Cl 9.81, N 19.39, S 8.85%

2-Acetylphenothiazine-tetracyanoethylene complex (III–V). A solution of III (0.480 g, 20 mmol) in ether (25 mL) was slowly added to the solution of V (0.260 g, 20 mmol) in ether (25 mL). Yield 82%, m.p. 130–135°C.
Elemental analysis; Found: C 65.16, H 2.84, N 18.89, S 8.46%
Calculated for $C_{20}H_{11}N_5OS$: C 65.04, H 2.98, N 18.97, S 8.67%

2-(Trifluoro)methylphenothiazine-tetracyanoethylene complex (IV–V). A solution of IV (0.540 g, 20 mmol) in ether (25 mL) was slowly added to the solution of V (0.260 mg, 20 mmol) in ether (25 mL). Yield 78%, m.p. 175–180°C.
Elemental analysis; Found: C 57.58, H 1.99, N 17.84, S 8.01%
Calculated for $C_{19}H_8N_5SF_3$: C 57.68, H 2.02, N 17.70, S 8.09%

Measurements. All the complexes were 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 CuK_α radiation. 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; reference - Al_2O_3; thermocouple - Platinum - Rhodium. The electronic absorption spectra and Reflectance spectra were recorded on Cary 2390 spectrophotometer. Infrared absorption spectra were recorded with Perkin-Elmer 783 spectrophotometer. ^1H NMR spectra were recorded on a JEOL FX-90Q FT NMR spectrometer. Electrical measurements were made on Wayne Kerr Automatic Precision Bridge B 905. For electrical measurements, the pellets were prepared at a pressure ~15 K bar 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 10 KHz and 1 KHz at different temperatures in the range (303–373 K). The magnetic susceptibilities of the complexes were measured on a Cahn Faraday balance at 10 K gauss magnetic field.

RESULTS AND DISCUSSION

Thermogravimetric studies. Thermal stability and decomposition characteristics: All of the phenothiazine-TCNE complexes reported in this paper were obtained as dark colored solids. The stoichiometries of these complexes were found to be 1:1 on the basis of their elemental and thermogravimetric analyses. Thermogravimetric and differential thermogravimetric curves of II–V system are shown in Figure 1. These curves show that the complexes are thermally stable up to 100°C but undergo two step decomposition at higher temperatures. First step of decomposition stoichiometrically corresponds to the loss of TCNE and the second one for the loss of phenothiazines. TG curve of II–V complex (Figure 1) shows that V is lost between 100–300°C, while II is lost between 300–660°C. The rate of decomposition is a maximum at 270°C for V and at 430°C for II, as indicated by its DTG curve (Figure 1). Similar curves were obtained for other complexes as well. These data led us to calculate the stoichiometry of the complexes and their decomposition characteristics. Since elemental analyses show 1:1 stoichiometry, the relative molecular mass of the complexes was calculated on this basis. The decomposition steps are as follows:

$$R - \text{TCNE} \longrightarrow R + \text{TCNE} \uparrow$$

$$R \longrightarrow R \uparrow$$

where R = I, II, III and IV. The calculated values are found in good agreement with the observed values. Thus, the phenothiazines-TCNE complexes have 1:1 stoichiometries and are thermally stable up to 100°C.

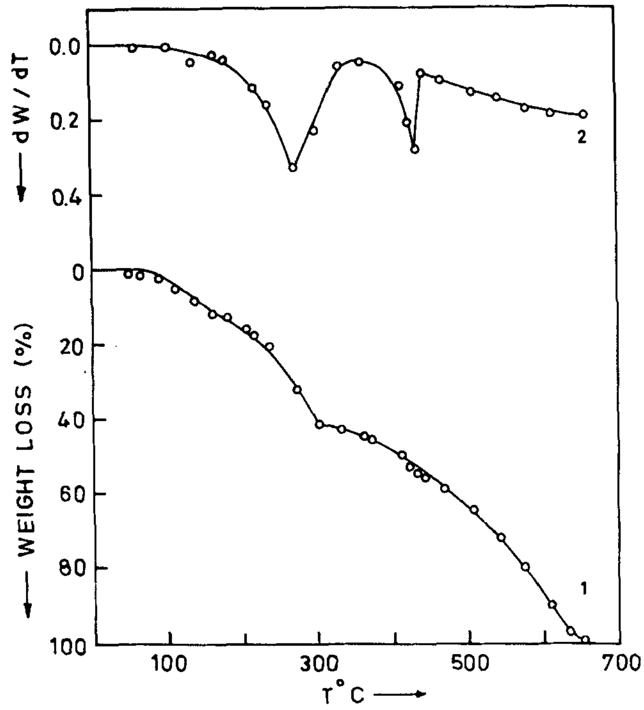


FIGURE 1 TG curve (1) and DTG curve (2) for 2-chlorophenothiazine-TCNE complex.

Structural Studies

The powder X-ray diffraction data for four phenothiazines-TCNE complexes are given in Tables I–IV, which were indexed by Ito's method.[11] The tables also include the normalized intensities, calculated and observed Q values ($1/d^2$) and corresponding Miller indices. The lattice parameters of single crystal of phenothiazine reported earlier were used as a guide in indexing the diffraction data.[12] The lattice parameters for different complexes are as follows:

(i) I–V: a 4.980 Å, b 8.580 Å, c 16.920 Å
(ii) II–V: a 4.720 Å, b 9.060 Å, c 22.975 Å
(iii) III–V: a 7.190 Å, b 12.980 Å, c 26.510 Å
(iv) IV–V: a 5.990 Å, b 10.590 Å, c 23.276 Å

The crystal systems of all these complexes have been found to be orthorhombic, similar to the crystal structures of the pure donors. This shows that the molecular frame-work of phenothiazines in their radical ion charge transfer salts with TCNE is similar to the pure donors which have been sufficiently established to be non-

TABLE I

Powder X-ray diffraction data of I–V charge-transfer complex

Powder pattern line	2θ	*d* values	Relative intensities	$Q_{(obs)}$	$Q_{(calc)}$	hkl
1	17.807	4.9810	79	0.0403	0.0403	100
2	20.715	4.2878	74	0.0544	0.0543	020,102
3	21.007	4.2289	86	0.0559	0.0559	004
4	21.440	4.1443	78	0.0582	0.0574	111
5	22.139	4.1151	87	0.0591	0.0578	021
6	23.232	3.8277	93	0.0683	0.0683	022,112
7	23.500	3.7856	89	0.0698	0.0695	014
8	25.730	3.4612	100	0.0835	0.0853	113

TABLE II

Powder X-ray diffraction data of II–V charge-transfer complex

Powder pattern line	2θ	*d* values	Relative intensities	$Q_{(obs)}$	$Q_{(calc)}$	hkl
1	7.694	11.4907	100	0.0076	0.0076	002
2	18.816	4.7161	49	0.0450	0.0449	100
3	19.589	4.5317	16	0.0487	0.0487	020
4	22.052	4.0308	12	0.0615	0.0595	015
5	23.283	3.8203	20	0.0685	0.0682	006
6	24.272	3.6668	12	0.0744	0.0741	113
7	25.057	3.5537	22	0.0792	0.0790	024,016
8	26.904	3.3138	27	0.0911	0.0928	007
9	28.056	3.1803	17	0.0989	0.1012	122
10	29.365	3.0415	19	0.1081	0.1096	030
11	30.549	2.9262	14	0.1168	0.1169	026,032
12	32.601	2.7466	13	0.1326	0.1334	018

TABLE III

Powder X-ray diffraction data of III–V charge-transfer complex

Powder pattern line	2θ	*d* values	Relative intensities	$Q_{(obs)}$	$Q_{(calc)}$	hkl
1	6.671	13.2503	83	0.0057	0.0057	002
2	12.311	7.1894	47	0.0193	0.0193	100
3	13.640	6.4918	47	0.0237	0.0237	020
4	16.303	5.4368	31	0.0338	0.0356	005
5	17.149	5.1706	50	0.0374	0.0380	113
6	19.313	4.5958	79	0.0473	0.0480	114
7	19.814	4.4807	32	0.0498	0.0487	122
8	20.030	4.4329	37	0.0509	0.0513	006
9	22.448	3.9606	50	0.0637	0.0658	124
10	23.613	3.7676	100	0.0704	0.0706	106,007
11	24.307	3.6617	63	0.0746	0.0757	017,034,116
12	27.527	3.2402	69	0.0952	0.0950	040
13	29.008	3.0781	63	0.1055	0.1047	036
14	42.341	2.1346	20	0.2195	0.2194	062

TABLE IV

Powder X-ray diffraction data of IV–V charge-transfer complex

Powder pattern line	2θ	*d* values	Relative intensities	$Q_{(obs)}$	$Q_{(calc)}$	hkl
1	7.606	11.6227	55	0.0074	0.0074	002
2	14.797	5.9865	45	0.0279	0.0279	100
3	16.745	5.2944	30	0.0357	0.0357	020
4	19.328	4.5922	71	0.0474	0.0462	005
5	20.342	4.3655	87	0.0525	0.0523	023,113
6	20.934	4.2434	48	0.0555	0.0551	015
7	21.076	4.2152	39	0.0563	0.0575	104
8	21.927	4.0034	29	0.0624	0.0636	120
9	23.273	3.8220	100	0.0685	0.0666	006,114
10	23.449	3.7937	64	0.0695	0.0710	122
11	23.955	3.7146	33	0.0725	0.0741	105
12	24.636	3.6136	37	0.0766	0.0755	016
13	25.551	3.4862	34	0.0823	0.0821	031,025,115
14	26.717	3.3366	34	0.0898	0.0906	007
15	27.744	3.2154	70	0.0967	0.0969	033,106
16	28.604	3.1207	62	0.1027	0.1034	026,116
17	29.658	3.0121	51	0.1102	0.1099	034,125
18	30.194	2.9998	30	0.1111	0.1115	200
19	31.746	2.8186	22	0.1259	0.1263	027,035
20	36.532	2.3364	27	0.1832	0.1855	029
21	39.973	2.2554	28	0.1966	0.1987	038

planar. Thus, it is clear that the ionic molecular complexes of phenothiazines containing their radical cations have non-planar geometries having mixed stacking in solid state. The lattice constants of naphthalene-TCNE complex have been reported to be as follows: a 7.26 Å, b 12.69 Å and c 7.21 Å; and lattice constants of perylene-TCNE as: a 15.70 Å, b 8.28 Å and c 7.31 Å having orthorhombic

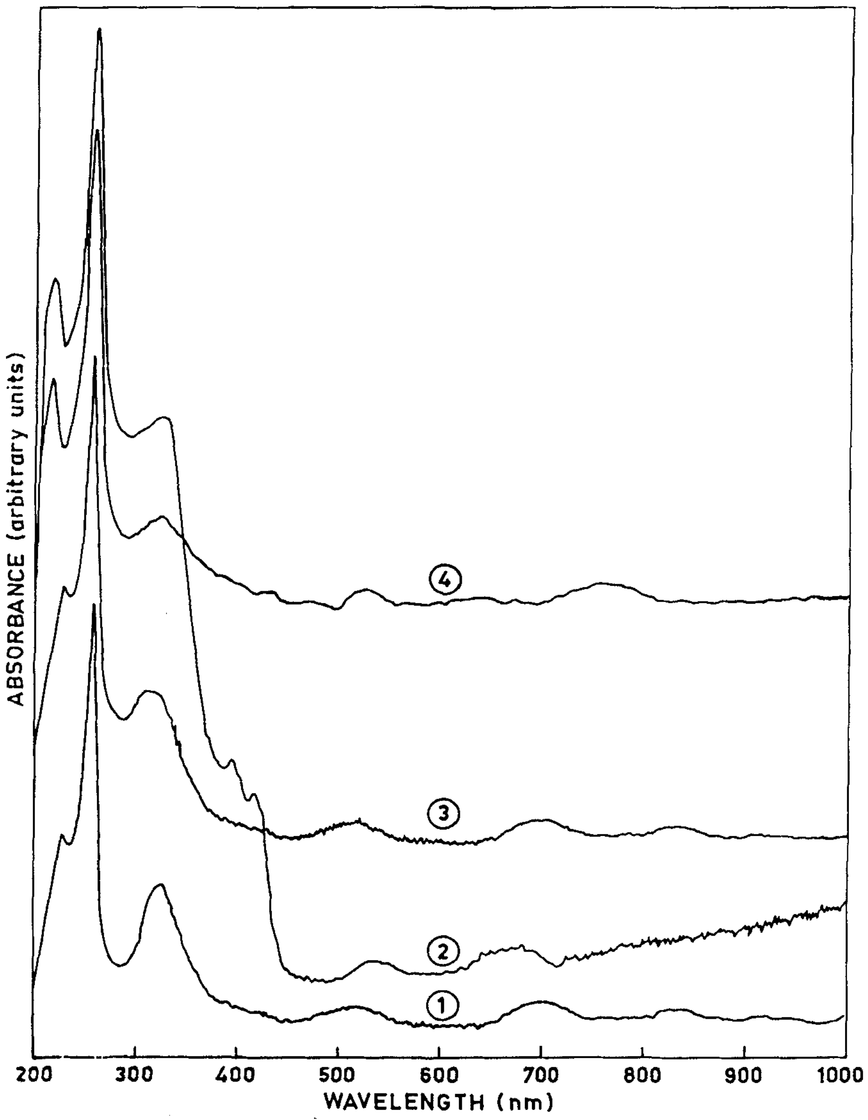


FIGURE 2 Electronic spectra of phenothiazine-TCNE (1), 2-chlorophenothiazine-TCNE (2), 2-acetylphenothiazine-TCNE (3) and 2-(trifluoro)methylphenothiazine-TCNE (4) complexes in nujol.

crystal structures.[13] Our values of a, b and c are quite different from the above, but they all have the same crystal structure. Orthorhombic crystal structures have also been found for the TCNE complexes with ferrocenes.[8]

Spectral Studies

a) Electronic and reflectance spectra. Electronic spectra of complexes in nujol have been reported in Figure 2. The electronic spectral bands for I–V complex were found at 12.12×10^3, 14.71×10^3, 19.61×10^3, 23.81×10^3, 30.77×10^3

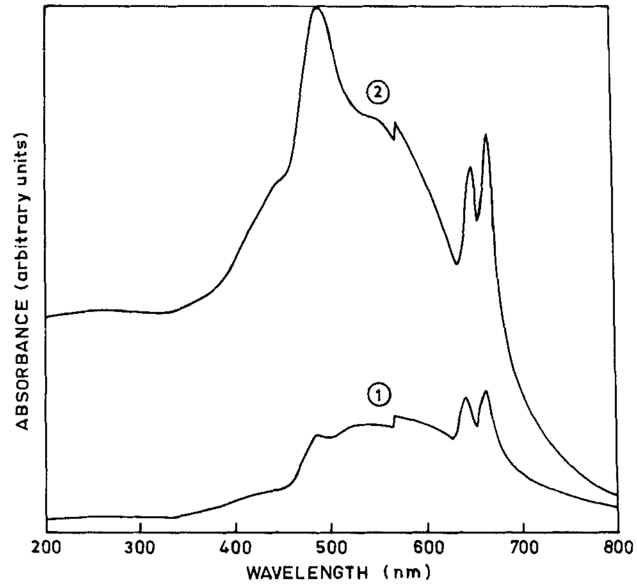


FIGURE 3 Reflectance spectra of 2-acetylphenothiazine-TCNE (1) and 2-chlorophenothiazine-TCNE (2) complexes.

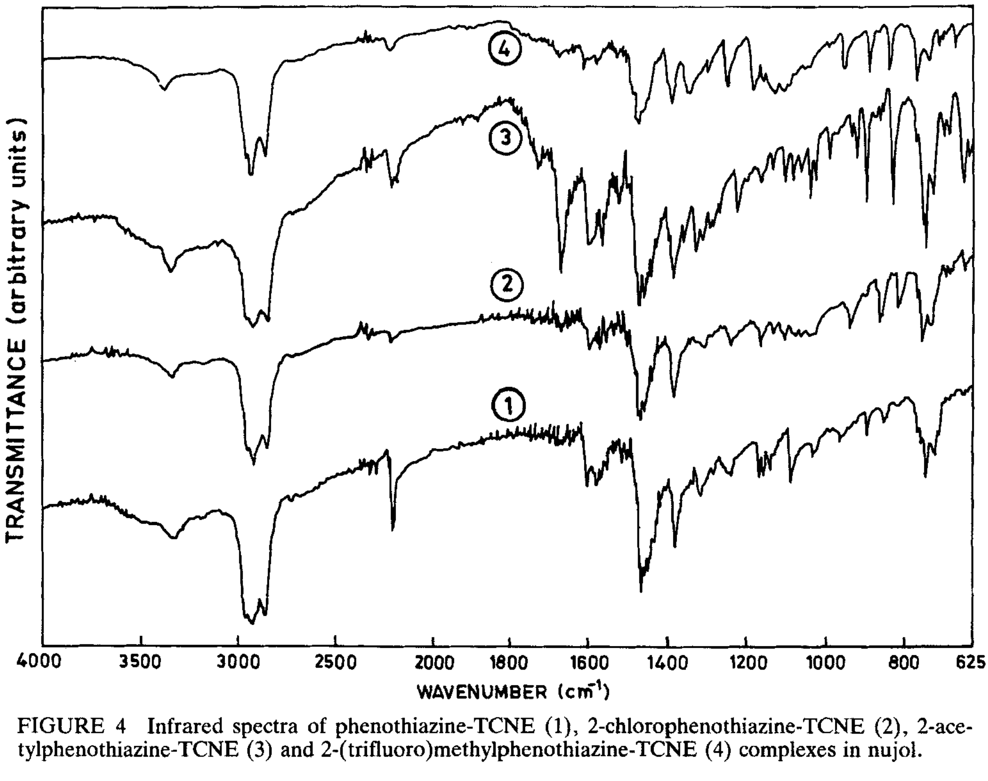


FIGURE 4 Infrared spectra of phenothiazine-TCNE (1), 2-chlorophenothiazine-TCNE (2), 2-acetylphenothiazine-TCNE (3) and 2-(trifluoro)methylphenothiazine-TCNE (4) complexes in nujol.

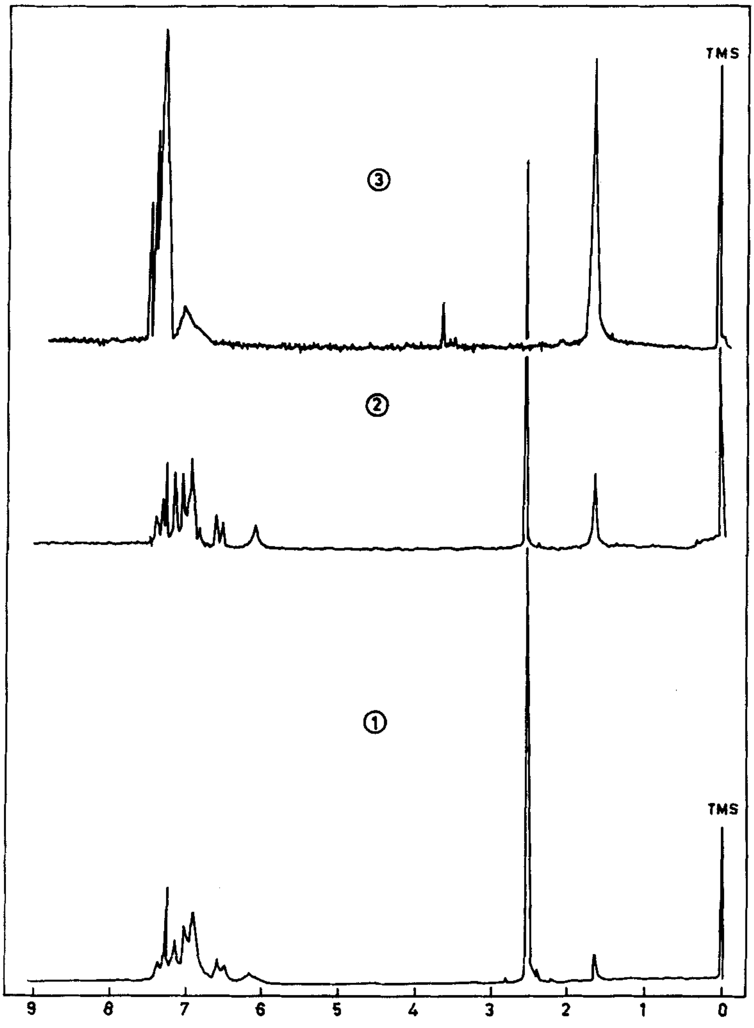


FIGURE 5 ^{1}H NMR spectra of 2-acetyl phenothiazine(1), 2-acetylphenothiazine-TCNE complex (2) and phenothiazine-TCNE complex (3).

and 39.22 × 10^3 cm^{-1}; for II–V, at 14.71 × 10^3, 18.87 × 10^3, 23.81 × 10^3, 25.00 × 10^3 and 38.46 × 10^3 cm^{-1}; for III–V, at 12.12 × 10^3, 15.15 × 10^3, 20.00 × 10^3, 25.00 × 10^3, 31.25 × 10^3 and 40.00 × 10^3 cm^{-1} and for IV–V, at 13.33 × 10^3, 20.00 × 10^3, 21.28 × 10^3, 22.73 × 10^3, 30.77 × 10^3 and 38.46 × 10^3 cm^{-1}. The diffuse reflectance spectra of these complexes have been presented in Figure 3. They showed bands at 14.93 × 10^3, 15.63 × 10^3 and 20.83 × 10^3 cm^{-1} for II–V and III–V systems, respectively.

The electronic absorption spectra of 1:1 complexes of arylamines with TCNE in dichloromethane exhibit two absorbance bands, the low wavelength maxima at 25.97 × 10^3 – 24.10 × 10^3 cm^{-1} and the high wavelength maxima at 17.24 × 10^3 – 12.20 × 10^3 cm^{-1}.[14] The charge-transfer spectra of substituted benzene donors

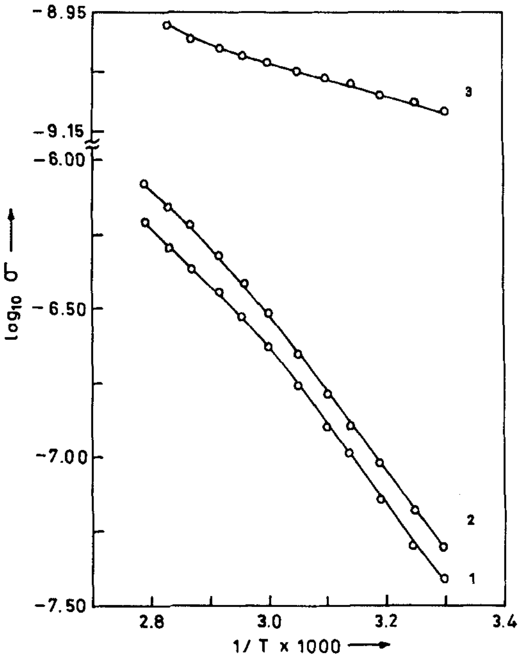


FIGURE 6 Log of conductivities as a function of inverse temperature for phenothiazine-TCNE complex at 1 KHz (1), at 10 KHz (2) and for 2-(trifluoro)methylphenothiazine-TCNE complex at 10 KHz (3).

with TCNE as acceptor showed both single and double charge-transfer bands.[15] Triphenyl borane, tri-*o*-tolylborane and trimesitylborane formed 1:1 colored complexes with TCNE, in which the triarylborane donated π-electrons from its phenyl rings to the vacant antibonding orbital of TCNE. The absorbance maxima were found at 23.81 × 10^3 and 19.23 × 10^3 cm^{-1}.[16] The electronic spectra of $[TCNE]^{-\cdot}$ $[Co(C_5Me_5)_2]^{+\cdot}$ has structured visible transitions at 23.38 × 10^3 cm^{-1} for $[TCNE]^-$ resulting from internal transition.[10] The charge transfer band for phenothiazine-TCNE complex have been reported at 11.74 × 10^3 cm^{-1} by Bhat.[17] Phenothiazine cations have characteristic electronic absorptions at 14.7 × 10^3 and 19.6 × 10^3 cm^{-1}.[18]

Based on these data, the existence of cation radicals of phenothiazine moieties and anion radical of TCNE have been proposed. However, electronic bands around 5000 cm^{-1} characteristic of interstack charge transfer were not observed.

b) Vibrational spectra. The vibrational spectra of various phenothiazines-TCNE complexes in nujol have been shown in Figure 4. The vibrational spectra of these complexes confirm their ion-radical character. Both the —NH peak for phenothiazines at around 3320 cm^{-1}–3380 cm^{-1} and C≡N peak at 2260 cm^{-1} for TCNE are shifted by 20–40 cm^{-1} and 50 cm^{-1}, respectively. This indicates a dative nature for the complexes.

The I.R. spectrum of polyacetylene doped with TCNE-benzene solution showed bands at 1370 and 900 cm^{-1}.[19] The spectrum of the $(CH)_x$ film exhibited the $\nu(C{\equiv}N)$ vibration mode at 2190 cm^{-1} which is shifted with respect to the 2260,

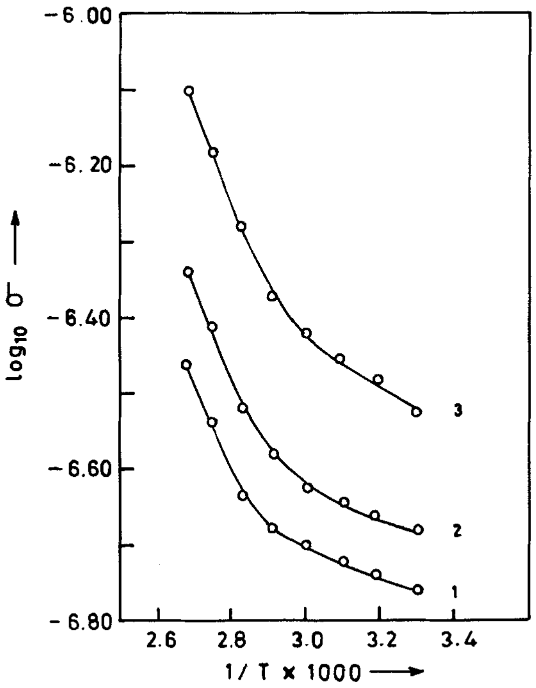


FIGURE 7 Log of conductivities as a function of inverse temperature for 2-chlorophenothiazine-TCNE complex at 100 Hz (1), at 1 KHz (2) and at 10 KHz (3).

2220 cm^{-1} $\nu(C{\equiv}N)$ doublet of pure TCNE. The weak C—C mode at 1135 cm^{-1} was shifted with respect to the 1155 cm^{-1} in the TCNE spectrum. The dichroic behavior of activated acceptor modes in pentamethylbenzene-TCNE and hexamethylbenzene-TCNE complexes has been observed by Stanley *et al.*[20] They observed that the spectra of the anion salts like $K^+TCNE^{\dot{-}}$ and $Na^+TCNE^{\dot{-}}$were highly dissimilar to the spectrum of TCNE. The most interesting new features in $K^+TCNE^{\dot{-}}$ spectrum were the intense band at 1371 cm^{-1} and the absence of absorption in the 600–1300 cm^{-1} region where the strongest TCNE fundamental absorption occurs. A very intense doublet was observed at 2180–2201 cm^{-1} for $\nu C{\equiv}N$ stretching mode. The infrared spectra of $[TCNE]^{\dot{-}}$ in presence of decamethyl-ferrocene and cobaltocene showed two $\nu C{\equiv}N$ stretching bands at 2144 and 2183 cm^{-1}.[10]

From this discussion, it is concluded that phenothiazines-TCNE complexes are of the dative type in which phenothiazines exist as cation radicals and TCNE as an anion radical.

c) ^1H NMR spectra. The ^1H NMR spectra of these complexes in $CDCl_3$ have been shown in Figure 5. It is observed that there is a large shift in 'H-intra' protons but 'H-extra' protons of phenothiazines remain as such. The replacement of complex aromatic multiplets of pure donors by singlets/doublets also supports that cation radicals may have many canonical forms yielding identical protons.

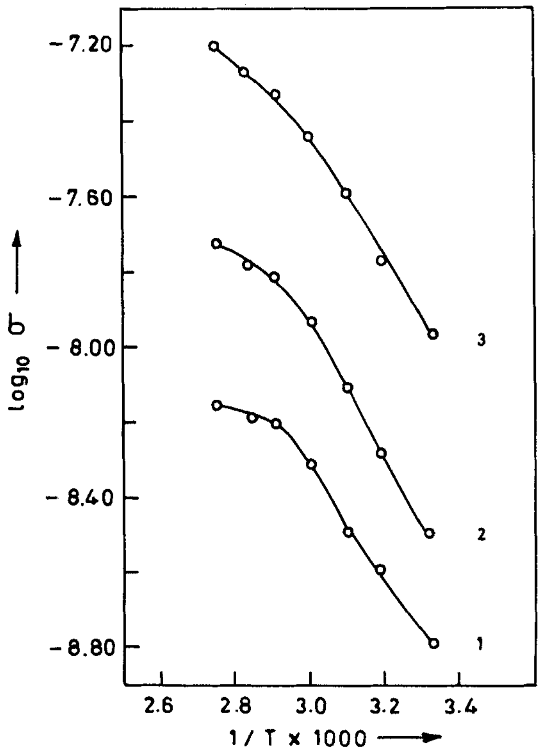


FIGURE 8 Log of conductivities as a function of inverse temperature for 2-acetyl phenothiazine-TCNE complex at 100 Hz (1), at 1 KHz (2) and at 10 KHz (3).

Electrical Properties

The electrical conductance of solid complexes of TCNE with phenothiazines in the form of pressed pellets at 10 KHz, 1 KHz and 100 Hz in the temperature range of 303 K and 373 K have been presented in Figures 6–8. The electrical conductivities of I–V and III–V complexes were found in the range of 10^{-8} to 10^{-9} S cm^{-1} and of II–V complex are of the order of 10^{-7} S cm^{-1}. The electrical conductivities of the IV–V complex are of the order of 10^{-10} S cm^{-1} or below 10^{-10} S cm^{-1}. These complexes show typical organic semiconductor behavior as for other phenothiazine complexes having discontinuities at particular temperatures as shown in Figures 6–8. The room temperature electrical conductivities of the complexes have been presented in Table V. The energy of activation determined from the slopes of two linear portions have also been presented in Table V, they have been labelled as E_{a_1} and E_{a_2}. E_{a_2} has been found to be higher than E_{a_1}, but both the values are characteristic of organic semiconductors. The low conductivity values may be attributed to mixed stacking of donors and acceptors and discontinuities to changes in conductivity mechanism. Thus, phenothiazines-TCNE complexes reported here are typical molecular semiconductors.

The dielectric constant values calculated from the measured capacitances have also been reported in Table V. They have been found to decrease with increasing

TABLE V

Electrical properties of charge transfer complexes of TCNE with some substituted phenothiazines

Complexes	Electrical conductivities at r.t. (30°C) and at 10 KHz, 1 KHz and 100 Hz freq. (10^{-8} S cm^{-1})			Capacitances at r.t. (30°C) and at 10 KHz, 1 KHz and 100 Hz freq. (pF)			Energy of activation for electrical conductivity at 10 KHz freq. (eV)		Dielectric constants at r.t. (30°C) and at 10 KHz, 1 KHz and 100 Hz freq.		
	10 KHz	1 KHz	100 Hz	10 KHz	1 KHz	100 Hz	E_{a_1}	E_{a_2}	10 KHz	1 KHz	100 Hz
I–V	5.01	3.89	0.10	9.95	15.10	34.30	0.40	0.51	25.42	38.58	87.63
II–V	29.20	20.86	17.51	15.13	34.88	132.49	0.23	0.06	151.24	348.66	1324.4
III–V	1.10	0.32	0.16	8.56	11.05	16.36	0.16	0.40	11.85	15.30	22.65
IV–V	0.08	—	—	5.90	—	—	0.12	—	8.54	—	—

frequency, typical of organic semiconductors, capacitive contributions being shorted at higher frequencies.[21]

Magnetic Properties

TCNE complexes with ferrocenes show interesting magnetic properties. But none of the complexes except IV–V show any measurable change in weight on application of magnetic field (10 K gauss) at room temperature. The change in weight for IV–V system is only 0.13 mg in about 58.74 mg of the sample. The magnetic susceptibility calculated for IV–V system at 32°C has been found to be 150×10^{-6} cgs unit which gives an effective magnetic moment of 0.61 BM. Similar values have been reported for ferrocene-TCNE charge transfer complex (0.63 BM).[22] These values are much lower than expected for the radical ion species present in these molecular semiconductors. This may be possibly due to strong antiferromagnetic interactions between radical ions. We could not probe it further for want of low temperature magnetic susceptibility measurement facility. Therefore, these compounds are diamagnetic/weakly paramagnetic possibly due to strong antiferromagnetic interactions between radical ions.

In conclusion, we can say that the phenothiazines-TCNE charge transfer complexes are molecular semiconductors with low electrical conductivities, two activation energies and diamagnetic. They are thermally stable up to 100°C. The crystal structures are orthorhombic.

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