

Electrical resistivity studies of certain quasi one-dimensional organic systems at high pressures and low temperatures

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Abstract. We report the electrical resistivity studies of six quasi one-dimensional organic systems under high pressures up to 8 GPa and temperatures down to 77K. The room temperature resistivity of these complexes lies in the wide range from 10^8 ohm cm to 0.05 ohm cm, but they have common features under high pressures. The possible interpretations of these behaviours have also been discussed.

Keywords. Electrical resistivity; quasi one-dimensional conductors; organic system; high pressures; low temperatures.

1. Introduction

The effect of high pressure on the electrical resistivity of organic quasi one-dimensional systems has aroused considerable interest in recent times, particularly after the discovery of superconductivity in the organic system $(\text{TMTSF})_2\text{-PF}_6$ (Jeromé *et al* 1980). It is realized that in order to understand the effect of high pressures on these organic systems, one needs to study them systematically and on a wide variety of samples.

The present paper reports the electrical resistivity studies of six charge transfer complexes and radical ion salts under high pressures up to 8 giga pascals (GPa) and temperatures down to 77K. The samples are tetramethyl *p*-phenylenediamine-tetracyano-quinodimethane (TMPD-TCNQ), tetramethylbenzidine-chloranil (TMBine-chloranil), benzidine-tetracyanoquinodimethane (Bine-TCNQ), tetramethylbenzidine-tetracyanoquinodimethane (TMBine-TCNQ), pyridinium-(tetracyanoquinodimethane)₂ [Py-(TCNQ)₂] and acridinium—(tetracyanoquinodimethane)₂ [AD-(TCNQ)₂]. It has been reported (Andre' *et al* 1976) that depending on their chemical structure, these molecules are categorized in two different classes—the dative structure and the segregated structure. The first four complexes have dative structure while the other two are of segregated structure.

2. Experimental details

The crystals were grown by the conventional solution techniques. They were characterized by first examining the composition through elemental analyses and then through the optical absorption spectra. The x-ray diffraction patterns for powder

samples were taken to verify the crystal structures. The details of the crystal growth and characterization have been given by Bandyopadhyay (1981) and Hemamalini *et al* (1981).

The high pressure experiments were carried out in a clamp-type-high pressure cell. The cell consists of a pair of Bridgman anvils made of tungsten carbide with 3% cobalt binder and has a tip of diameter 4 mm. Heat treated pyrophyllite is used as gasket material and steatite is used as the pressure transmitting medium. The details of high pressure arrangement and calibrations both at room temperature and at low temperatures are given by Bandyopadhyay *et al* (1980b).

Experiments were carried out on both the single crystals and the compacted pellets. The pellets were made by powdering the materials and pressing the powder in a die. The conventional four-probe and two-probe methods were used for these measurements with a Keithley constant current source (model no. 225) and a digital electrometer (model no. 616) as the measuring instruments.

3. Results and discussions

The electrical resistivity and the anisotropy of these six crystals are given in table 1. These values agree quite well with the earlier values reported in the references given in table 1. At room temperature, the electrical resistivities of all the six compounds have been studied up to the pressures 8 GPa in either single crystal form or in the pellet form. The behaviour of these complexes under high pressure is nearly the same—namely, a drastic drop in resistivity in the low pressure range (below 1.5 GPa) but above that pressure there is a marked tendency towards saturation in resistivity. As an example figure 1 shows the normalized resistivity *versus* pressure curves of the TMBine-chloranil compound both perpendicular and parallel to the chain direction and in the pellet form. It is to be noted here that in all the high resistive samples, the drop in resistivity is more than 10^3 times. In the low resistive samples, the drop is also very low—of the order of 5 times. Figure 2 shows the normalized resistivity *versus* pressure of Py-(TCNQ)₂ in the single crystal form and in the pellet form, as an example of the low resistivity samples (Bandyopadhyay *et al* 1981).

It is interesting to note that all the high resistive samples have dative structure which essentially means the overlap is between a donor and an acceptor molecule, whereas

Table 1. Electrical resistivity and anisotropy of the crystals

Systems	Resistivity (Ω cm)	Anisotropy	References
1. TMPD-TCNQ	10^9	10–20	Somoano <i>et al</i> (1975)
2. TMBine-chloranil	10^7	10–20	Matsunaga and Saite (1971)
3. Bine-TCNQ	10^8	10–20	Ohmasa <i>et al</i> (1971)
4. TMBine-TCNQ	10^5	100	Bandyopadhyay <i>et al</i> (1979); Ohmasa <i>et al</i> (1971)
5. Py-(TCNQ) ₂	15	100	Baspalov and Titov (1975); Holczer <i>et al</i> (1977)
6. Ad-(TCNQ) ₂	0.05	100	Holczer <i>et al</i> (1978); Shchegolev (1972)

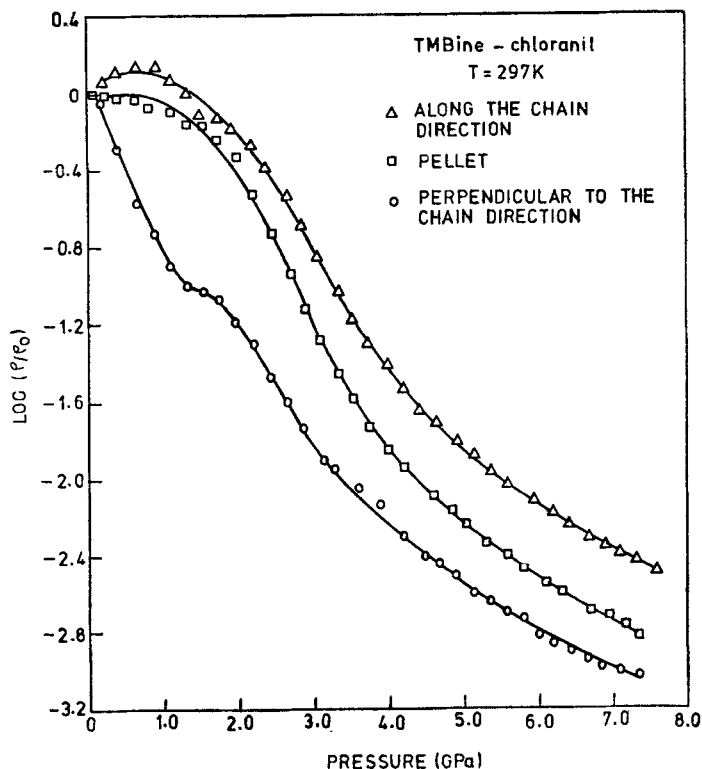


Figure 1. Normalized resistivity versus pressure of TMbine-chloranil at room temperature.

the low resistive samples have segregated structure which indicates the overlap between the donor or the acceptor molecules. The reasonable high conductivity of these organic molecules arises from the overlap of the molecular orbitals which cause delocalization of the π -electron along the axis of the stacking. The difference between the ionization potential of the donor and the electron affinity of the acceptor is fairly large; thus in the dative structure molecules the overlap is very small and as a result the resistivity is fairly high. In the segregated structure, the resistivity is very small. With the enhancement of pressure, the overlap increases and as a result the effective band gap decreases. It is to be mentioned here that some compounds form inclusion compounds with the solvent medium. For example Bine-TCNQ (dichloromethane) (Ohmasa *et al* 1971) forms an inclusion compound in the solvent dichloromethane. The behaviour under high pressure of this inclusion compound is quite different from the solvent free, Bine-TCNQ (Bandyopadhyay and Subramanyam 1981).

In order to find the amount of band gap, low temperature experiments at different clamped pressures have been carried out on all these six compounds. Two types of behaviours have been observed in these compounds. In the system like TMPD-TCNQ or Py-(TCNQ)₂, the activation energy is found to be changing with temperature, while in the other TMbine-TCNQ, TMbine-chloranil or Bine-TCNQ and Ad-(TCNQ)₂, the activation energy is independent of temperature. Figures 3, 4 show the $\ln(\rho/\rho_0)$ versus $1000/T$ curves at different clamped pressures for TMPD-TCNQ and TMbine-TCNQ as examples of their behaviour (Bandyopadhyay 1981;

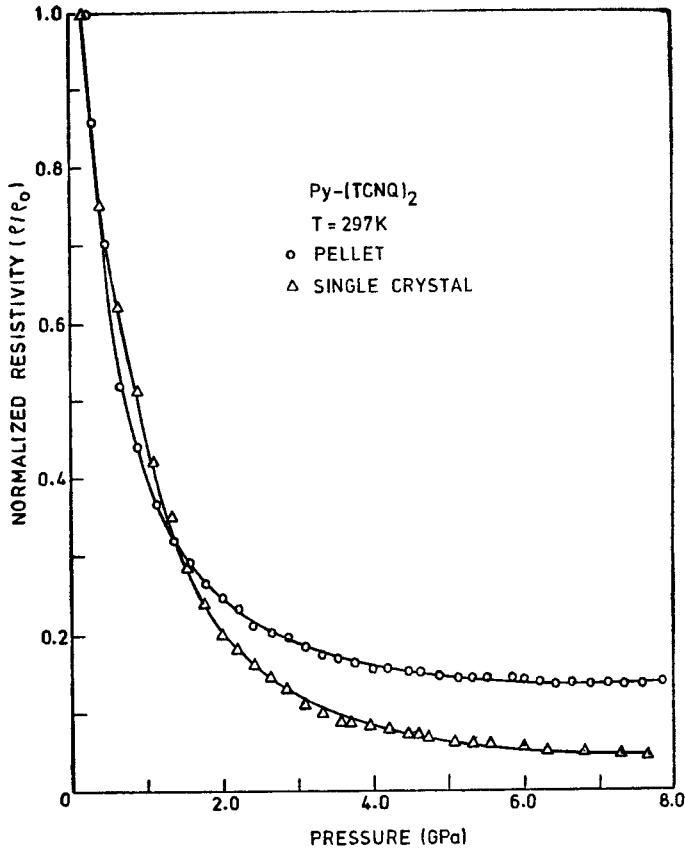


Figure 2. Normalized resistivity versus pressure of Py-(TCNQ)₂ at room temperature.

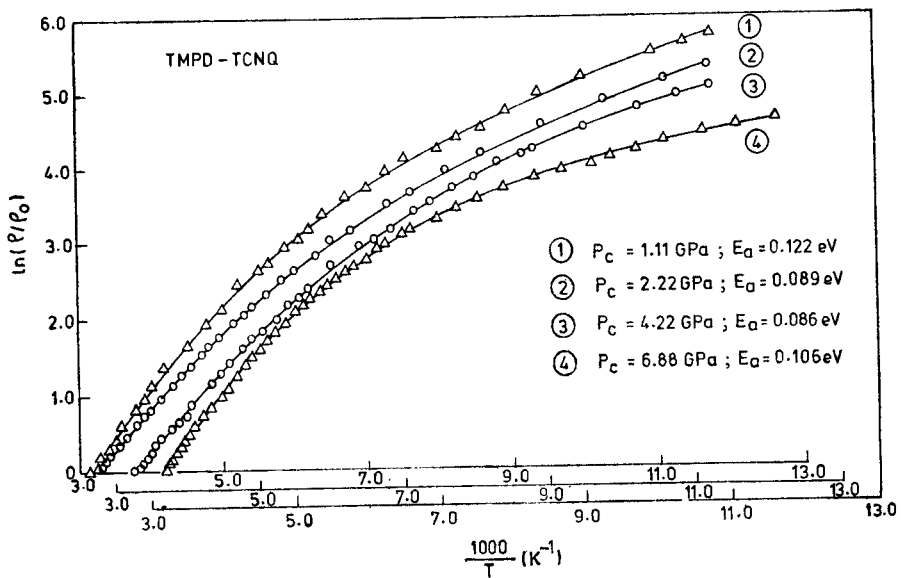


Figure 3. $\ln(\rho/\rho_0)$ versus $1000/T$ at different clamped pressures of TMPD-TCNQ.

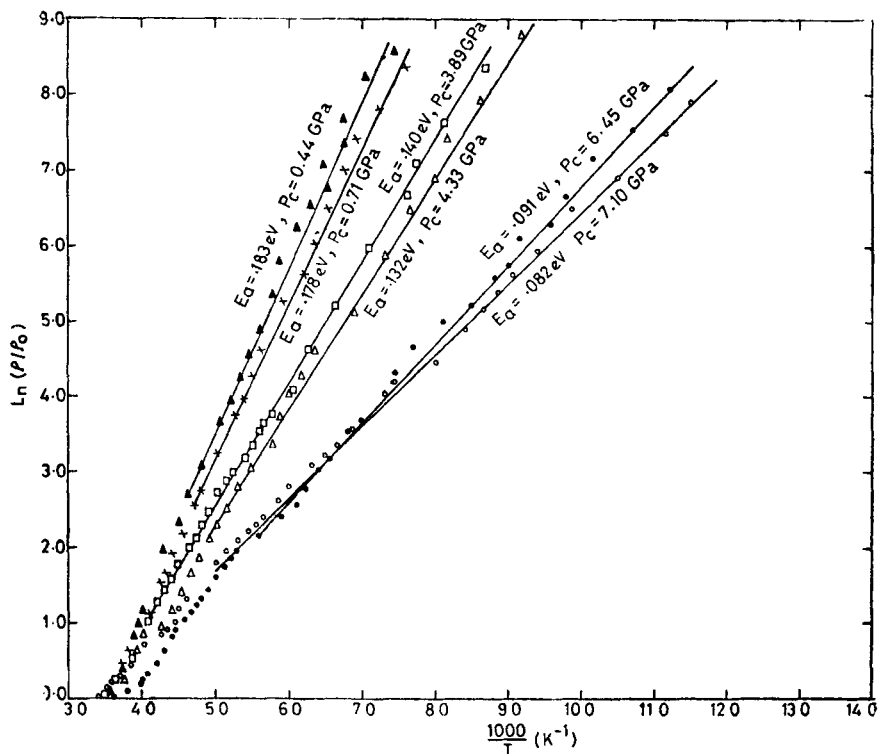


Figure 4. $\ln(\rho/\rho_0)$ versus $1000/T$ at different clamped pressures of TMBine-TCNQ.

Table 2. Activation energy at different clamped pressures

Sample	Clamped pressure (GPa)	Activation energy (eV)
TMPD-TCNQ	1.11	0.122
	2.22	0.089
	4.22	0.086
	6.88	0.106
TMBine-TCNQ	0.44	0.188
	0.71	0.178
	3.89	0.140
	4.33	0.132
	6.45	0.091
	7.10	0.082
Bine-TCNQ	2.22	0.130
	3.33	0.100
	4.44	0.070
TMBine-chloranil	1.78	0.263
	3.77	0.222
	5.77	0.192
Py-(TCNQ) ₂	1.11	0.058
	2.23	0.057
	6.77	0.042
Ad-(TCNQ) ₂	1.11	0.029
	2.66	0.027
	5.77	0.020

Bandyopadhyay *et al* 1979). Table 2 shows the activation energy at different clamped pressures of all the systems. It is clear from the table that the activation energy decreases with pressure in all the systems irrespective of the behaviour at low temperatures.

In order to explain the effect of high pressure on these compounds, an approximate calculation has been carried out by Bandyopadhyay (1981). The band structures of these complexes are not known. However, for dative structure compounds, x-ray diffraction studies confirm that the conducting chain consists of alternative donor and acceptor molecules. The observed anisotropy in resistivity in the stacking direction is due to the large overlap of the orbitals of the molecules in comparison with that in other directions. It is assumed that the chains are not interacting. According to this approximation, the electronic conductivity is expressed in the tight binding approximation as,

$$\sigma = \sigma_0 \exp(-V_{\text{eff}}/kT), \quad (1)$$

where V_{eff} is the effective band gap which can be written as

$$V_{\text{eff}} = (E_a - E_d) + \left\{ \int \phi_a^*(r) V_a(r-a) \phi_a(r) dr - \int \phi_d^*(r) V_d(r-a) \phi_d(r) dr \right\}, \quad (2)$$

where E_a and E_d are the electron affinity of the acceptor and the ionization potential of the donor respectively; ϕ_a and ϕ_d represent the atomic wave functions of the acceptor and the donor molecules; $V_d(r)$ and $V_a(r)$ represent the atomic potential fields of the donor and the acceptor respectively and a is the interatomic distance. With the increase in pressure, the interatomic distance a decreases. This decrease is linear in the low pressure region. As the pressure increases, non-linear higher order terms come into play. This is because at these pressures steric hindrance dominates and prevents a further decrease in the interatomic distance. As a result there will be a stiffening effect in the lattice. Thus in order to include all these terms, the change in interatomic distance is expressed by

$$\Delta a(p) = a(p) - a_0 = a_1 p + a_2 p^2 + a_3 p^3, \quad (3)$$

where a_1 , a_2 and a_3 are the constants and are directly related to the elastic constants of different orders.

Similarly, the effective band gap (V_{eff}) can be written, neglecting the higher order terms, as

$$V_{\text{eff}} = V_{\text{eff}}^0 - \lambda p, \quad (4)$$

where V_{eff}^0 is the normal band gap and λ is a constant. A linear term is found to be adequate over the pressure region under consideration. If we assume that the overlap is symmetrical,

$$\sigma_0 = At^2, \quad (5)$$

where t is the overlap integral represented by

$$t = t_0 \exp(-\eta a), \quad (6)$$

where η is a constant. Substituting all these equations in (1), one can obtain,

$$\rho = 1/\sigma = \rho_0 \exp(\alpha p + \beta p^2 + \nu p^3), \quad (7)$$

where $\rho_0 = [\exp(2\eta a_0 + V_{\text{eff}}^0/kT)]/At_0^2$;

$$\alpha = 2\eta a_1 - (\lambda/kT); \quad \beta = 2\eta a_2 \text{ and } \gamma = 2\eta a_3.$$

In the segregated structures also, one arrives at the same sort of expression as (7).

An attempt has been made to fit the experimental data points for all the crystals to the above equation. The curve-fitting was carried out in a multivariate search procedure in the least square sense (Bandyopadhyay 1981; Bandyopadhyay *et al* 1980a). The standard deviation is found to be 10^{-4} . The values of these constants for the six compounds are shown in table 3. Knowing α , β and γ , one can obtain a_1 , a_2 and a_3 . From these values of α , β and γ , it can be said that for the high resistive samples, the overlap is small. The overlap in this case increases much faster with pressure than in the case of low resistive samples. This has been indicated in figure 5 where $1/\rho_0$ ($d\rho/dP$) is plotted against pressure for all the samples.

Next, one must consider whether the band gap collapses and gives rise to a metallic state at high pressures. Earlier studies by Bentley and Drickamer (1963) on thirteen charge transfer complexes and Aust *et al* (1964) on quinolinium-(TCNQ)₂, etc. complexes under high pressure, indicate that in some of the complexes the resistivity increases (irreversibly) above a certain pressure after reaching saturation. Therefore, the metallic state cannot be achieved. However, in systems like HMTTF-TCNQ, (TMTSF)₂-PF₆, TTF-TCNQ (Bechgaard *et al* 1980; Jeromé *et al* 1980) etc. high pressure generally suppresses the Peierls transition and stabilizes the metallic phase even at low temperature. The low temperature behaviours of these six complexes show that the conduction process is activated. So the question of stabilization of metallic state does not arise.

In the sample TMPD-TCNQ, low temperature studies at different clamped pressures show that there exists a strong deviation from the linear behaviour. The temperature at which the deviation has been found, is nearly in the same range. This was

Table 3. The values of the constants for the different structures of the crystals

Structure	Sample (crystals)	α (GPa) ⁻¹	β (GPa) ⁻²	ν (GPa) ⁻³
Dative	Bine-TCNQ	-1.81226	1.67271×10^{-1}	-4.63383×10^{-3}
	TMBine-chloranil	-3.58684	6.98850×10^{-1}	-4.93336×10^{-2}
	TMBine-TCNQ	-3.39565	4.65672×10^{-1}	-2.50082×10^{-2}
	TMPD-TCNQ	-1.12190	1.94207×10^{-1}	-1.02851×10^{-2}
Segregated	Py-(TCNQ) ₂	-1.17302	1.50562×10^{-1}	-7.20759×10^{-3}
	Ad-(TCNQ) ₂	-1.06622	1.80896×10^{-1}	-1.37641×10^{-2}

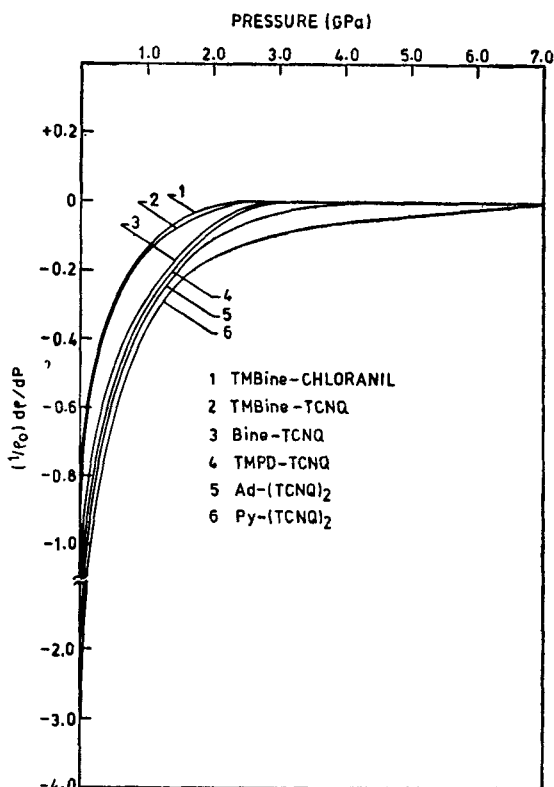


Figure 5. $(1/\rho_0) dp/dp$ versus pressure.

earlier observed in both the electrical and the magnetic studies at normal atmospheric pressure (Somoano *et al* 1975) and there the sharp break was attributed to a set of magnetic transitions (Etemad and Ehenfreund 1972). The detailed nature of the magnetic transition is not very clear. However, in $\text{Py}-(\text{TCNQ})_2$ two drastic changes in activation energy one at a temperature of 150K and the other one at 80K at normal atmospheric pressure have been reported by Holczer *et al* (1977). The first one has been attributed to a first order phase transition due to a small change in the lattice parameter while the second one is the crossover from the singlet-triplet state to a one-dimensional Heisenberg state. The first one at 150K has been observed at all clamped pressures. This has been attributed to the manifestation of the same phase transition as has been observed in normal atmospheric pressure, although the exact effect of high pressures on the first order transition is not very clear. In the other four samples, the activation energy is found to be independent of temperature. This is a normal property of intrinsic semiconductors.

4. Conclusion

All the above experimental observations can be explained only qualitatively in view of the severe limitations of our understanding of the exact effect of high pressures on these organic complexes. The situation can be improved in future by studies which can give information on various processes.

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