

Electrical resistivity of a quasi-one-dimensional organic system under high pressure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 L307

(<http://iopscience.iop.org/0953-8984/4/21/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:14

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Electrical resistivity of a quasi-one-dimensional organic system under high pressure

Yadunath Singh, D P Goswami, M Bala and M L Kalra

Department of Physics, College of Science, M L Sukhadia University, Udaipur—313 001, India

Received 16 March 1992

Abstract. We report on the electrical resistivity of a quasi-one-dimensional organic system having asymmetric donor molecules like quinolinium under high pressure up to 8 GPa at room temperature. A low-temperature resistivity study at normal pressure has also been made. The single crystals were grown by an electrochemical process. The pressure studies reveal that there is a strong negative pressure derivative of resistivity in the low-pressure region, but at high pressures there is a marked tendency towards saturation.

Organic materials have been primarily regarded as electric insulators. The mobility of electrons and its underlying mechanism as well as the synthesis of materials of higher conductivity in organic crystals began to draw the attention of scientists during the last decade, and became a 'hot' subject. A high concentration of current carriers observed in TCNQ (7,7,8,8-tetracyano-p-quinodimethane) salts and the extraordinarily high electrical conductivity found in TTF-TCNQ strengthened the interest in organic conductors—along with the possibility of fluctuating superconductivity at higher critical temperatures. This can be investigated by noting the consequences of modifying the structure, either chemically or physically, by applying pressure to affect the intermolecular spacings [1-5]. In the present paper we report a study of the resistivity of quinolinium-TCNQ at pressures up to 8 GPa. Achieving an understanding of the basic conduction mechanism under high pressure in the system, on the basis of experimental results, is our aim.

There are three methods generally used for growing the crystals. The most commonly used one is the recrystallization of the final complex in a solvent medium [6, 7]. The second is the slow diffusion technique [8] and the third one, used by us, is the electrochemical technique [9]. Needle-like bluish crystals of dimensions $10 \times 0.01 \times 0.01 \text{ mm}^3$ were obtained by this process. Initially both donor and acceptor compounds are purified by recrystallization in acetonitrile. Warm solutions of both are poured into separate arms of an H-type tube. The middle arm of the tube is separated by a sintered glass disc, number 2. One platinum electrode is dipped into each arm, and connected to the terminals of a battery, acting like an anode and like a cathode in the donor and acceptor solutions, respectively. A current of 3-4 mA was passed through the solution for three days. Good pure crystals appear after washing with chloroform. The product is characterized using elemental analysis, atomic spectra, infrared spectra and x-ray diffraction patterns.

In tables 1 and 2 we give the data on the microanalysis and the main infrared peaks of the charge-transfer compounds, respectively. The absorption spectrum of $\text{Qn}-(\text{TCNQ})_2$ in acetone exhibits major maxima at 844 and 822 and minor bands at 762, 744, 680 and 665 μm , which indicate complete transfer of electrons from Qn and TCNQ^{2-} ion formation. The infrared spectra of the complex, shown in figures 1(a) and 1(b), show the $\text{C}\equiv\text{N}$ band at 2180 (ms, sp) cm^{-1} with 40 cm^{-1} negative shift and the $\text{C}=\text{C}$ band at 1510 (m, sp) cm^{-1} with 30 cm^{-1} negative shift. The skeletal bands of the quinoid ring almost disappear. The appearance of new bands at 1650 (m, br), 1620 (m, br) and 1100 (s, v, br) cm^{-1} indicates the presence of a benzenoid ring structure [10].

Table 1. Data on the microanalysis of the charge-transfer compound.

Complex		% of C	% of H	% of N
TCNQ	Calculated	70.58	1.96	27.45
	Found	70.56	1.95	27.48
$\text{Qn}(\text{TCNQ})_2$	Calculated	73.70	2.79	32.46
	Found	73.70	2.73	32.48

Table 2. The main infrared peaks of the organic charge-transfer compound, in cm^{-1} .

Complex	$\text{C}\equiv\text{N}$	$\text{C}=\text{C}$	Quinoid skeletal bands	Benzenoid skeletal bands
TCNQ	2220 (s, sp)	1540 (s, sp)	1350 (s, sp)	—
			1130 (m, sp)	—
			960 (m, sp)	—
			860 (vs, sp)	—
$\text{Qn}(\text{TCNQ})_2$	2180 (ms, sp)	1510 (m, sp)	—	1650 (m, br)
			—	1620 (m, br)
			—	1100 (s, vbr)

The x-ray powder diffraction pattern was taken to verify the structure of the complex. The essential idea is to index the diffraction peaks with the help of known cell parameters and then compare the systematic absence of different planes with reported data [11]. The segregated structure of $\text{Qn}(\text{TCNQ})_2$ is confirmed by the above studies.

The pressure experiment was carried out in the clamp-type cell shown in figure 2. 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. The details of the high-pressure arrangement and its calibration are given in [12]. The cell is pressurized in a hydraulic press to any desired pressure up to 80 kbar. The cell is calibrated at room temperature for pressure measurement against the polymorphine phase transition of bismuth and ytterbium [13, 14]. The usual four-probe method shown in figure 3 was used for electrical resistivity measurements with a Keithley constant-current source, digital electrometer and Keithley null detector microvoltmeter. Measurements of the resistivity versus temperature were also performed on the sample at normal pressure. The behaviour is shown in figure 4. Prior to measurement, the flat surfaces of the sample at the probes were covered with silver paste to ensure good electrical contacts. To minimise

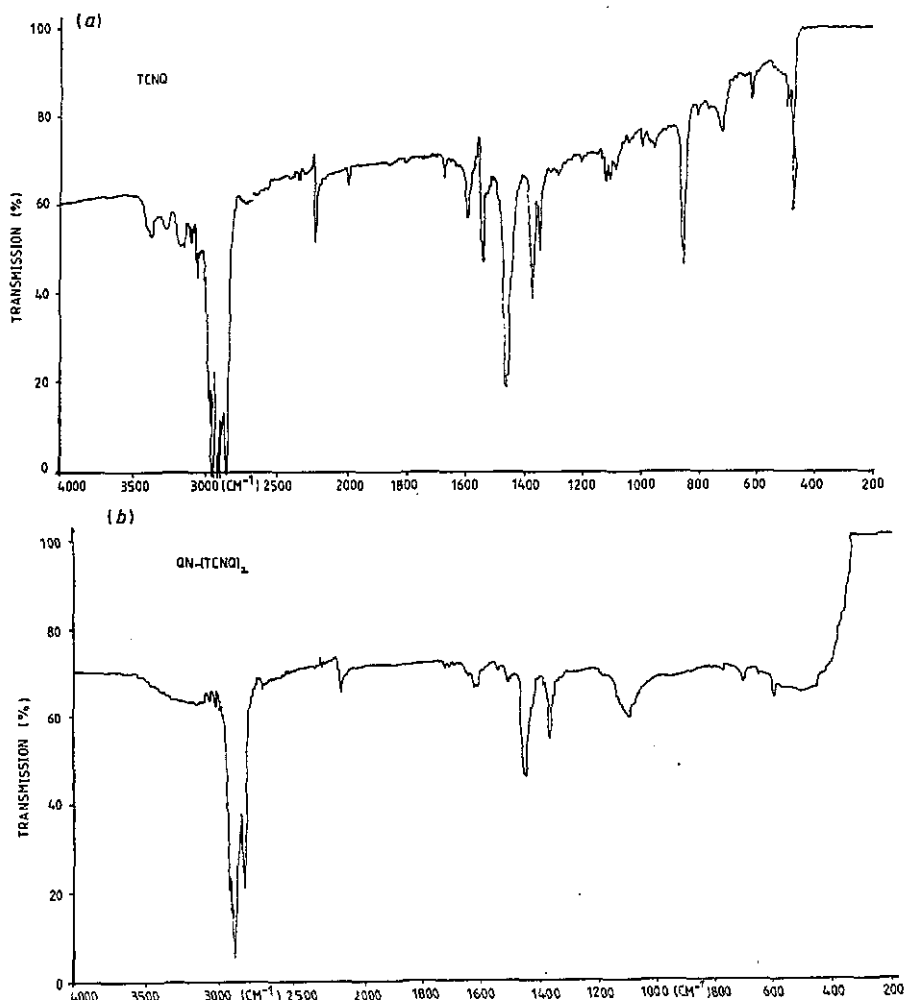


Figure 1. (a) Infrared spectra of TCNQ at 300 K. (b) Infrared spectra of Qn-(TCNQ)₂ at 300 K.

the adsorption of gases on the sample, the complete measuring device was connected to a high-vacuum cryostat. Care was taken to avoid the undesirable temperature gradient. The measurements were performed in such a way that the temperature of the sample was held uniform. There are two main difficulties in measuring the conductivity of organic charge-transfer salts. First, the crystals are extremely fragile and also one has to avoid large contact resistance. This means that great care must be taken in sample mounting, and the four-probe method must be used. Secondly, the available crystals are small and Joule heating of the sample may occur at relatively low power; hence large currents should not be allowed to flow through the crystal.

Figure 5 shows the normalized resistivity as a function of pressure. The resistivity is normalized with respect to that at normal atmospheric pressure. It is clear that there is a sudden drop of resistivity in the lower pressure region. However, as the pressure increases the rate of change of resistivity with pressure decreases. This means that as the pressure increases, non-linear higher-order terms come into play. This is

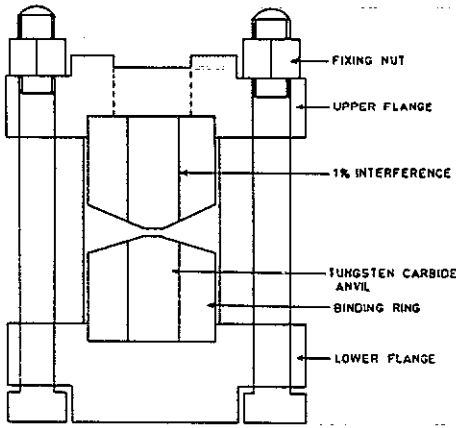


Figure 2. High-pressure clamp apparatus.

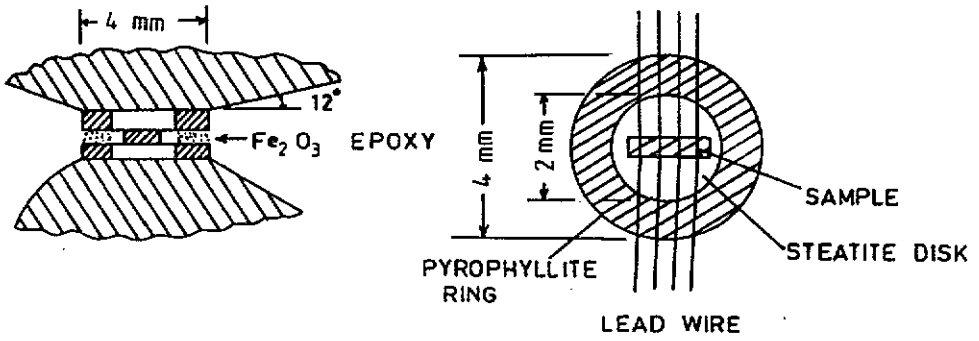


Figure 3. Sample assembly for the four-probe method.

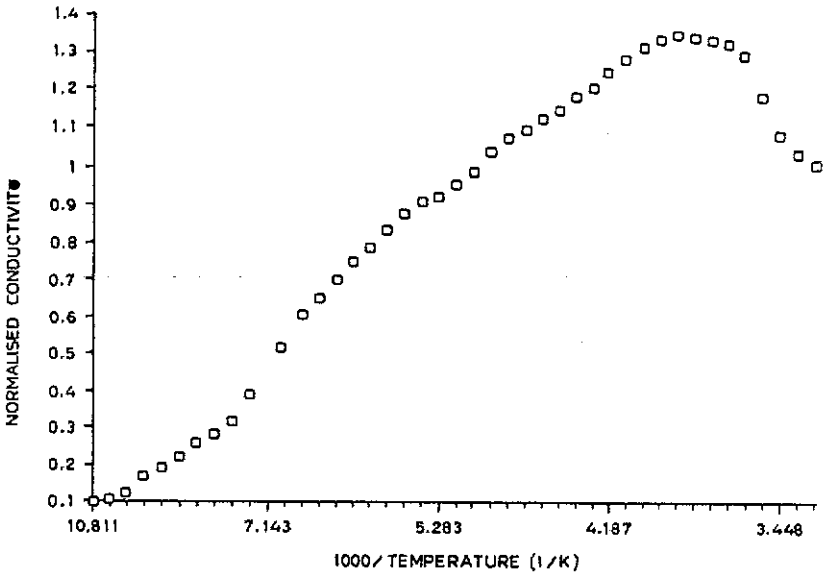


Figure 4. Temperature-dependent normalized conductivity σ/σ_{RT} .

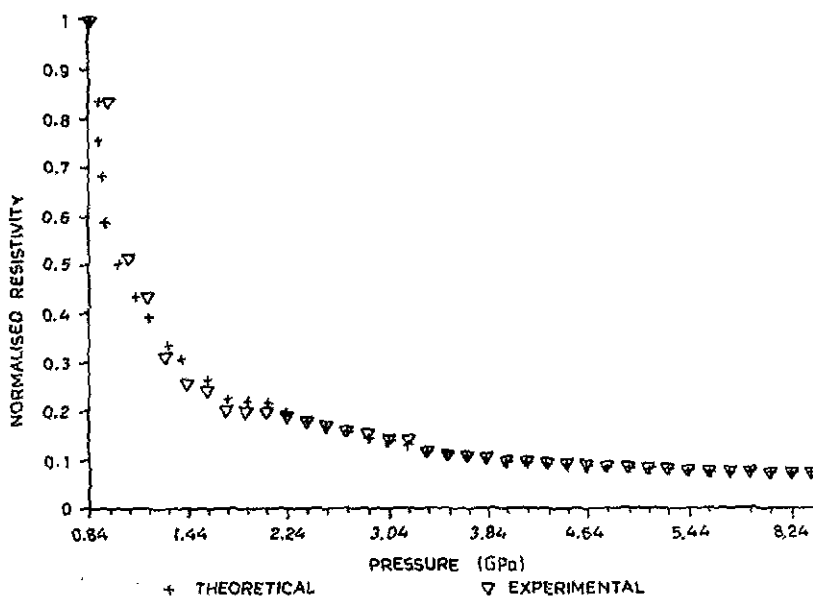


Figure 5. Pressure-dependent normalized resistivity of Qb-(TCNQ)₂ at 300 K.

because as the pressure increases steric hindrance starts dominating and prevents a further decrease of the interatomic distance and, obviously, there will be some effect of stiffening in the lattice. To explain the results obtained theoretically the electronic conductivity is expressed in the tight-binding approximation:

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

where V_{eff} is the effective band gap and the other symbols have their usual meanings.

In the presence of pressure at a particular temperature the resistivity can be given as [15]

$$\rho = 1/\sigma = \rho_0 \exp(\alpha P + \beta P^2 + \gamma P^3) \quad (2)$$

where $\rho_0 = [\exp(2\eta\alpha_0 + V_{\text{eff}}^0/kT)]/At_0^2$, with $\alpha = 2\eta\alpha_1 - \lambda/kT$, $\beta = 2\eta\alpha_2$ and $\gamma = 2\eta\alpha_3$. Here α , β and γ are constants related to the elastic constants of the system. Knowing α , β and γ , one can obtain α_1 , α_2 and α_3 . An attempt has been made to fit our data using equation (2). The values of the constants obtained from a least-squares curve-fitting method [16, 17] are given below.

Table 3.

Sample	α (GPa ⁻¹)	β (GPa ⁻²)	γ (GPa ⁻³)
Qb-(TCNQ) ₂	-0.9605041	1.13302×10^{-1}	-4.25206×10^{-3}

The orders of the constants obtained by us are in agreement with those obtained for other compounds having asymmetric donor molecules like Py-(TCNQ)₂ and Ad-(TCNQ)₂ [18]. It is found that the theoretical curve fits quite satisfactorily with the

experimental results. The resistivity of a single crystal as a function of temperature and at normal pressure is observed, and is shown in figure 3. The electrical resistivity study with pressure on the system clearly indicates that the resistivity decreases drastically within a very short pressure range. This tremendous decrease in resistivity is due to a large increase of charge-transfer forces within this pressure region, which may be due to a decrease in the interatomic distance and more overlap of orbitals along the chain. As the system studied is a disordered one-dimensional structure, all electronic states must be localized, justifying the use of the tight-binding approximation. However, wavefunctions are extended over several lattice sites along the chain [19]. As the pressure increases, the overlap of orbitals increases along the chain, and hence the probability of hopping of electrons between two adjacent sites also increases, decreasing the resistivity. An optical study of the system with pressure may throw more light on the discussion of the results given above.

The high-pressure study in this work was carried out at the Department of Physics, Indian Institute of Science, Bangalore. We would like to acknowledge the help of and fruitful discussions with Professor S V Subramanyam. One of the authors is grateful to Dr R Menon, Dr T R Ravindran and Mr R S Vaidyanathan for their cooperation in performing the experiment. The work was financially supported by the DST, New Delhi.

References

- [1] Little W A 1964 *Phys. Rev.* **134** A1416
- [2] Akamatsu H, Inokuchi H and Matsunaga Y 1954 *Nature* **173** 168
- [3] Kepler R G, Bierstedt P E and Merrifield R E 1960 *Phys. Rev. Lett.* **5** 503-4
- [4] Coleman L B *et al* 1973 *Solid State Commun.* **12** 1125
- [5] Keller H J (ed) 1974 *Low Dimensional Cooperative Phenomena* (New York: Plenum)
Devreese J T *et al* (ed) 1979 *Highly Conducting One Dimensional Solids* (New York: Plenum)
Alcacer L (ed) 1979 *The Physics and Chemistry of Low Dimensional Solids* (Dordrecht: Reidel)
Kagashima S, Nagasawa H and Sambongi T 1988 *One-Dimensional Conductors (Springer Series in Solid State Sciences 72)* (Berlin: Springer)
Ishiguro T and Yamaji K 1990 *Organic Superconductors (Springer Series in Solid State Sciences 88)* (Berlin: Springer)
- [6] Andre J J, Bieber A and Gautier F 1976 *Ann. Phys.* **10** 145
- [7] Melby L R *et al* 1962 *J. Am. Chem. Soc.* **84** 3374
- [8] Anzai H 1976 *J. Cryst. Growth* **33** 185-7
- [9] Williams J M *et al* 1985 *Prog. Inorg. Chem.* **35** 80
- [10] Luneli B *et al* 1970 *J. Chem. Phys.* **52** 2375
- [11] Kobayashi H, Marumo F and Saito Y 1971 *Acta. Crystallogr. B* **27** 373
- [12] Bandyopadhyay A K, Nalini A V, Gopal E S R and Subramanyam S V 1980 *Rev. Sci. Instrum.* **51** 136-9
- [13] Homan C G 1975 *J. Phys. Chem. Solids* **36** 1249
- [14] Fasol G and Schilling J S 1978 *Rev. Sci. Instrum.* **49** 1722
- [15] Bandyopadhyay A K *et al* 1980 *J. Phys. C: Solid State Phys.* **13** L803-7
- [16] Nelder J A and Meal R 1965 *Comput. J.* **7** 308
- [17] Balakrishnan N, Murthy P K and Ramakrishna S *IEEE Trans. Antennas Propag.* private communication: submitted
- [18] Bandyopadhyay A K *et al* 1981 *Chem. Scr.* **17** 47-8
- [19] Bloch A N, Werman R B and Varma C M 1972 *Phys. Rev. Lett.* **28** 753