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Low Temperature Structure and Physical Properties of *N*-Methyl,2,4-Dimethyl Pyridinium $(TCNQ)_2$

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The low-temperature (~ 173 K) structure of NMe2,4MePy$(TCNQ)_2$ was determined and compared with the room-temperature structure. Electrical, magnetic, dielectric, and spectroscopic properties of the salt are reported. Detailed discussion of the transport properties is presented in terms of a one-electron semiconductor model with low-temperature behaviour controlled by electrically active impurities.

INTRODUCTION

Recent extensive investigations on semiconducting organic solids based on substituted pyridinium cations and TCNQ anions[1–12] encouraged us to undertake many-sided studies of the complex TCNQ salt of *N*-methyl-2,4-dimethylpyridinium (NMe2,4MePy).† This salt differs

†In an earlier paper[15] we used a different abbreviation MDMP for the same cation.

from the majority of salts investigated so far by the asymmetrical substitution of the pyridinium cation. The small asymmetry may introduce disorder of the cations and thus change considerably the electrical transport properties. The purpose of the present studies was to investigate an interesting anomaly in the temperature dependence of the microwave conductivity, which is not shown in the d.c. conductivity measurements.[13]

SYNTHESIS AND CRYSTAL HABIT

Synthesis of the complex TCNQ salt of *N*-methyl-2, 4-dimethylpyridinium was carried out by the method of Melby *et al.*[14] *N*-methyl-2,4-dimethyl-pyridinium iodide was obtained by the reaction of methyl iodide with the corresponding pyridinium base. The commercial TCNQ was purified by sublimation and recrystallisation from acetonitrile.

Elementary analysis performed in a Perkin Elmer 240 instrument as well as IR and U.V./visible spectra confirmed that the salt had 1 : 2 stoichiometry.

The crystals of NMe2,4MePy(TCNQ)$_2$ grow in two different forms. One form includes comparatively large crystals, with dimensions about $4 \times 1 \times 0.3$ mm^3, with irregular, stratified surfaces. The other form consists of single needle-shaped crystals with well-defined flat surfaces and typical dimensions $2 \times 0.2 \times 0.1$ mm^3.

LOW-TEMPERATURE CRYSTAL STRUCTURE

The room-temperature structure of NMe2,4MePy(TCNQ)$_2$ needle-shaped crystals was described by us previously.[15] Now we present its low-temperature structure at 173 $\pm$ 10 K. The space group was shown to be the same as at room-temperature, by checking that the systematically absent reflections were not observed. The unit cell dimensions were determined by the least squares refinement of the diffractometer orientation matrix, fitting 25 observed peaks. 2300 intensities were collected on an Enraf Nonius CAD-4 computer-controlled, four-circle diffractometer, with an $\omega/.67\ \theta$ scan, a scintillation counter, and CuKα radiation (λ = 1.5418 Å). The intensities were corrected for Lorentz and polarisation factors, but not for absorption.

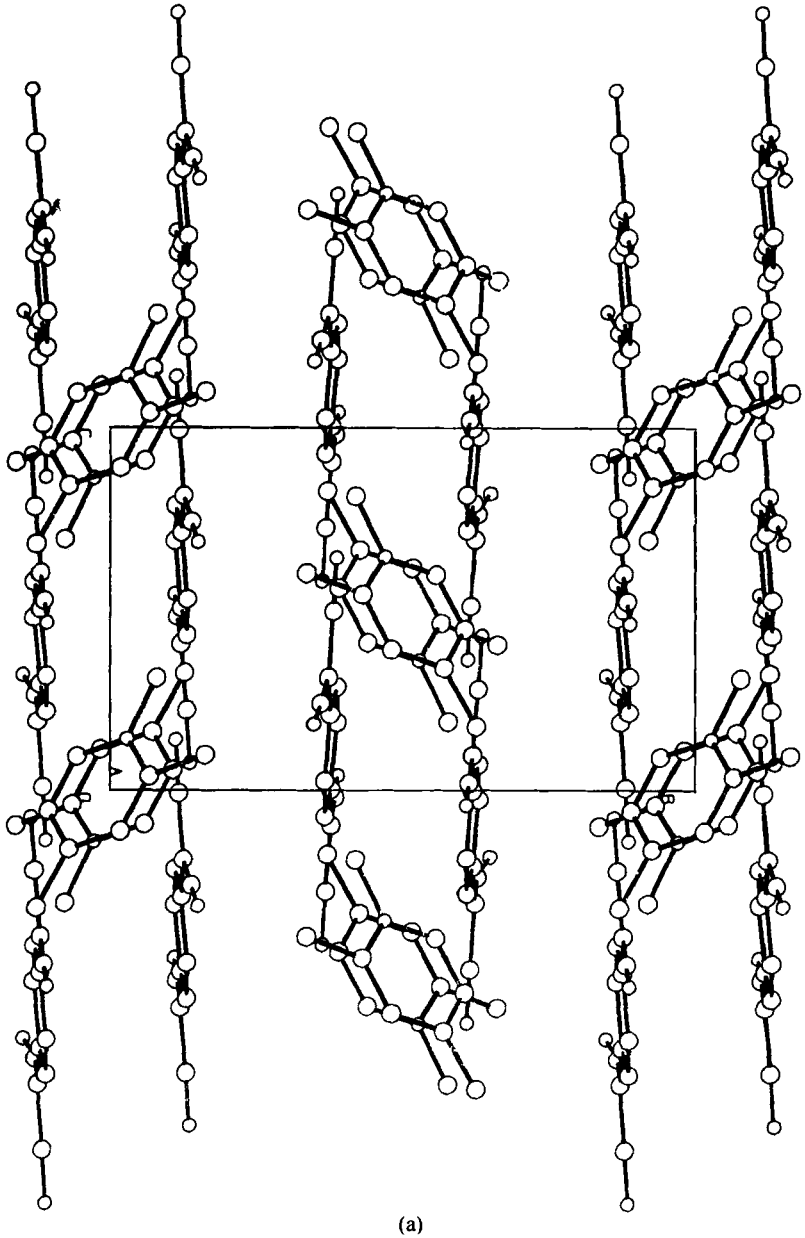
The crystal of NMe2,4MePy(TCNQ)$_2$ at low-temperature is also monoclinic, space group $P2_1/c$, with a = 13.721(3) Å, b = 12.705(7)

Å, $c = 7.811(6)$ Å, $\beta = 92.55\ (1)°$; $U = 1360(2)$ Å,^{3} $Z = 2$. One can see that the low temperature parameters are changed a little compared to room-temperature parameters, mainly as a result of contraction due to cooling. The differences expressed as a percentage of the room-temperature values are: $\Delta a/a = 0.5\%$, $\Delta b/b = 1.4\%$, $\Delta c/c = 0.5\%$, and $\Delta U/U = 2.4\%$.

Assuming the structure is essentially the same as that determined at room-temperature, the coordinates for the room-temperature structure were used as the starting-point for the refinement. 1532 significant reflections ($I > 3\sigma(I)$) were used to refine these positions. The dimensions of the cation were constrained to be the same as at room-temperature. This was thought reasonable, as cooling affects intermolecular interactions, rather than intramolecular dimensions. The thermal parameters of the TCNQ molecule atoms were allowed to refine anisotropically, while the cation refined isotropically. A weighting scheme was used, calculated in the form of a 5-term Chebyshev series, so as to make $w(|F_o| - |F_c|)^2$ as constant as possible over the whole $|F_o|$ range. After locating the H atoms approximately by means of a difference map, their idealized positions were derived and used in the calculation of structure factors without refinement. The final R value was .0660 for 1532 reflections.

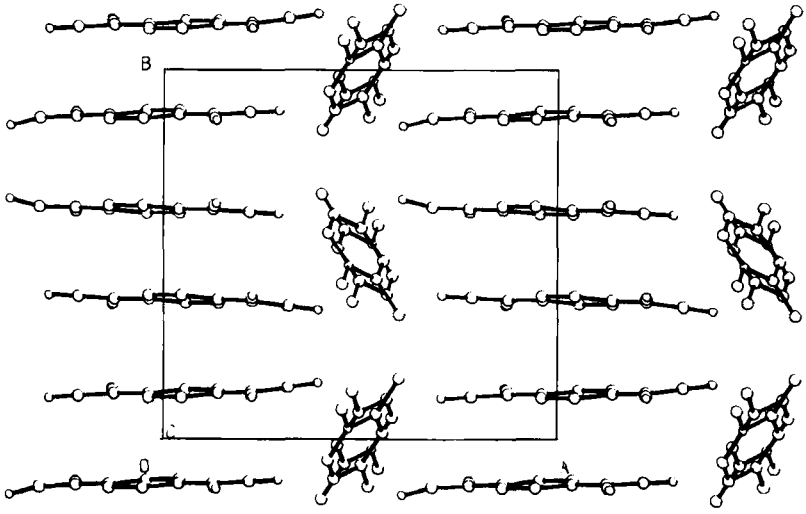
Figure 1 shows the structure of NMe2,4MePy(TCNQ)$_2$ projected along the a and c crystallographic axes. The essential features are the same as in the room temperature structure, with TCNQ's stacked plane-to-plane almost perpendicular to the b axis, and the cation occupying one of two centrosymmetrically-related positions in a disordered manner. The angles between the various least-squares best planes do not differ significantly from those calculated at room temperature. The differences of the perpendicular separations between the molecular planes, from those in the room temperature structure, expressed as a percentage of the room temperature values, are: intra-diad separation—1.5%, inter-diad separation—1.4%; the same separations calculated from planes of the atoms of the rings only are 1.4% and 1.8% respectively. It means that the interplanar separation within the diad is 3.14 Å, and between adjacent diads is about 3.54 Å.

The most significant difference, though, is the deviation of the centre of the cation from the centre of symmetry at $(\frac{1}{2}, 0, 0)$, this becoming 0.326 Å, a net decrease of 6.3% (low temperature cation centre at $x = 0.513$, $y = 0.021$, $z = 0.009$). The implication is that the cation has a tendency to draw towards the equilibrium position at the centre of the symmetry, in addition to the purely mechanical effect of contraction.



(a)

FIGURE 1 The structure of NMe2,4MePy(TCNQ)$_2$ at 173 ± 10 K along (a) the *a* crystallographic axis, (b) the *c* crystallographic axis.



(b)

FIGURE 1 (*Continued*)

Two separate runs were carried out, and the cell-constants were refined at various temperatures to check whether the change in cell-constants is linear. The graphs of cell-constants vs. temperature, show the change to be reasonably linear, within experimental error. By comparison of the points for increasing and decreasing temperatures, there is no evidence for any hysteresis in cell dimensions.

EXPERIMENTAL TECHNIQUES

The d.c. electrical conductivity, σ_{dc}, along the *a* axis of the single crystals was measured by the standard four-probe technique[11] whereas the microwave conductivity, σ_m, and the electrical permittivity, ϵ', were measured using the cavity perturbation method.[13,16] A device[12] similar to that described by Chaikin and Kwak[17] was used to measure the thermoelectric power *S*.

Spectroscopic investigation of NMe2,4MePy(TCNQ)$_2$ was performed in the intermediate infrared region, between 4000 and 200 cm^{-1}, using a Perkin Elmer spectrophotometer type 180 with temperature control. The samples were prepared by compressing the finely powdered salt with KBr (at a weight ratio of 1 : 1000). The range of the temperature measurement was from ambient to about 110 K.

The static magnetic susceptibility was determined by the Faraday method in the temperature range 2.5 to 300 K. The measurements were performed on polycrystalline samples, and the constant diamagnetic contribution was determined by the Pascal additivity rule and was -2.88×10^{-4} e.m.u./mole.

RESULTS

The d.c. electrical conductivity of the single needle-shaped crystals of NMe2,4MePy(TCNQ)$_2$ was measured along the *a* axis direction only. The temperature-dependence of σ_{dc} is shown in Figure 2; the points for increasing and decreasing temperature are indistinguishable. A characteristic feature of the conductivity in these salts resides in the change in activation energy with temperature. The high-temperature

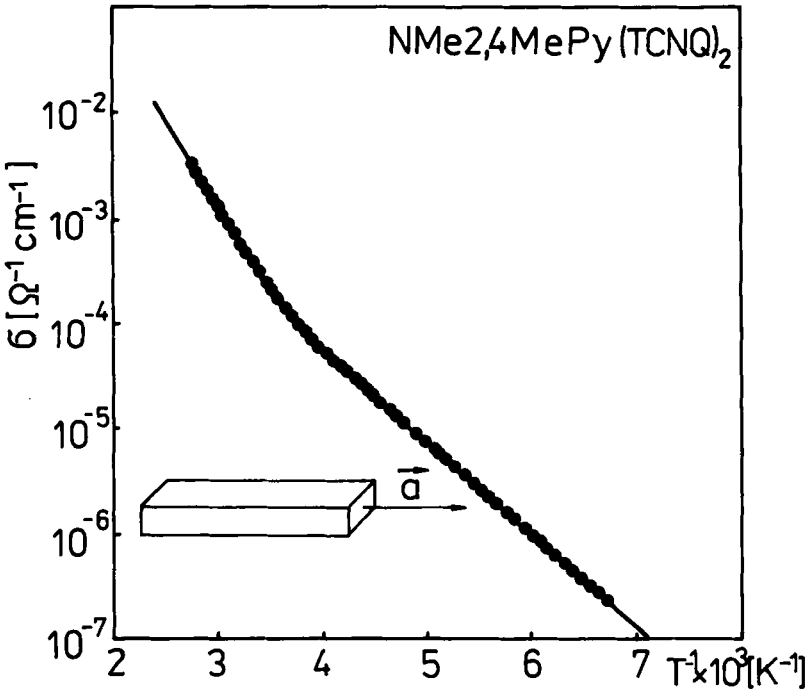


FIGURE 2 The single crystal d.c conductivity σ for NMe2,4MePy(TCNQ)$_2$ along the *a* axis. The line plotted is the best fit to equations discussed in the text.

conductivity can be described by the exponential function

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

with activation energy E_a of 0.33 eV, falling to 0.17 eV at low temperatures. The value of the room-temperature conductivity ($\sigma_{RT} = 3.5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$) as well as the activation energy values for NMe2,4MePy(TCNQ)$_2$ are similar to those previously reported for TCNQ complex salts with symmetrically-substituted methyl pyridinium cations[11]. The change of the activation energy occurs at a temperature of about 250 K. At approximately the same temperature the Seebeck coefficient changes its character (Figure 3). The Seebeck coefficient displays a strong temperature-dependence with an anomaly between 225 and 270 K. This anomaly is more clearly visible in Figure 4 showing the Peltier coefficient, Π.

The electric permittivity, ϵ', and microwave conductivity, σ_m, for relatively large irregular crystals of NMe2,4MePy(TCNQ)$_2$ taken from our previous paper[13] are shown in Figure 5. The temperature depen-

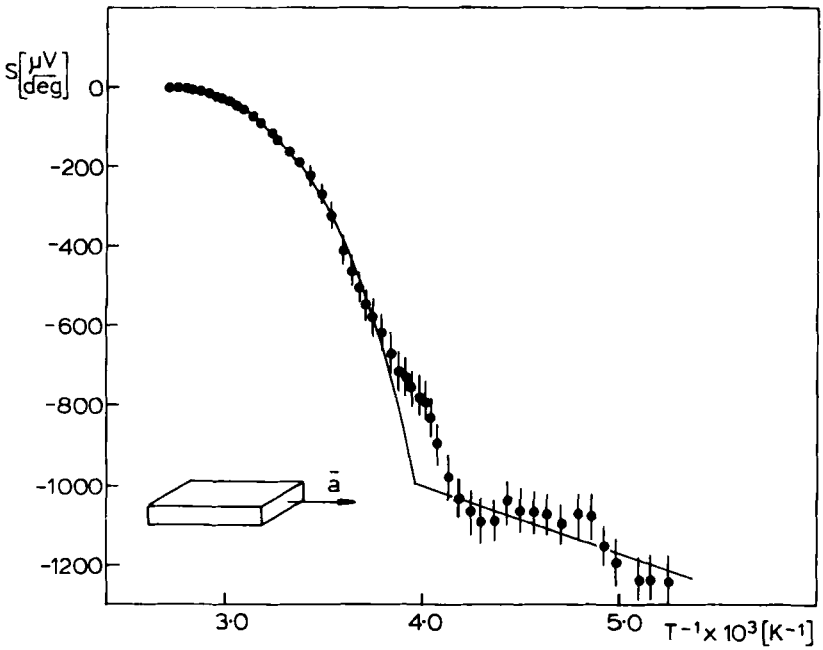


FIGURE 3 The Seebeck coefficient S along the a axis vs. $1/T$. The curve plotted is the best fit to equations discussed in the text.

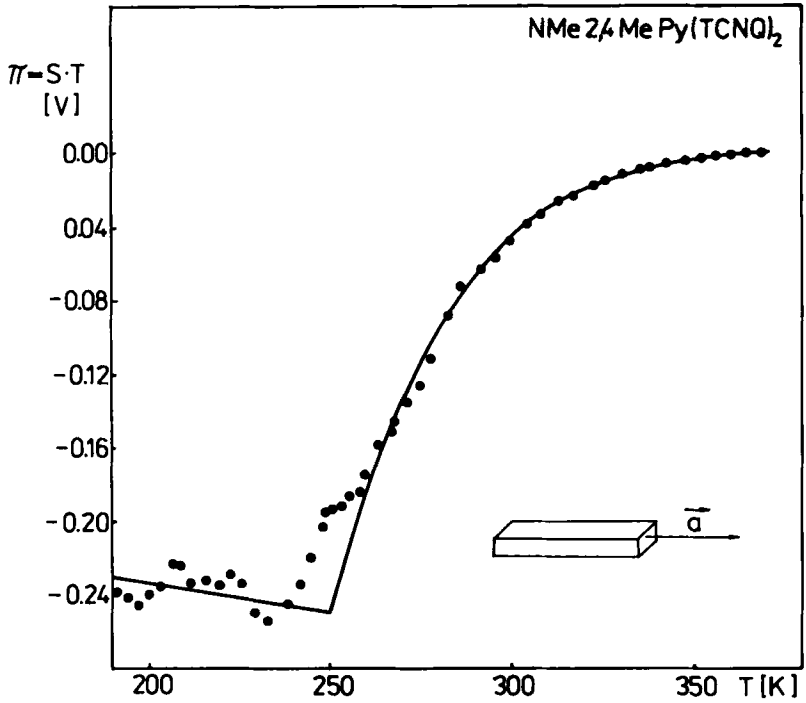


FIGURE 4 The Peltier coefficient Π for NMe2,4MePy(TCNQ)$_2$ along the *a* axis.

dence of the microwave conductivity, σ_m, shows an anomaly between 230 and 185 K. However, the electric permittivity, ϵ', as well as the d.c. conductivity, σ_{dc}, show normal temperature dependencies, without any anomalous changes.

The IR spectrum of NMe2,4MePy(TCNQ)$_2$ is typical for TCNQ complex salts. The absorption bands are situated in the wing of the charge transfer band ($\omega_{CT} \approx 4000$ cm^{-1}). The strongest absorption bands are those in which the A_g modes of the internal vibrations of TCNQ molecules are activated due to their coupling to the electron oscillations. These bands are rather broad and intense; this is characteristic for salts with partial charge transfer and is caused by a fluctuation of the electronic charge at each TCNQ molecule. The thermal evolution of the spectrum was studied by going up and down between the room temperature and 110 K. The changes of band intensities vs. temperature were rather weak, regular and reversible, without any anomalies or hysteresis.

The thermal variations of the paramagnetic susceptibility of the salt has been discussed previously.[18] It was shown that the spin suscep-

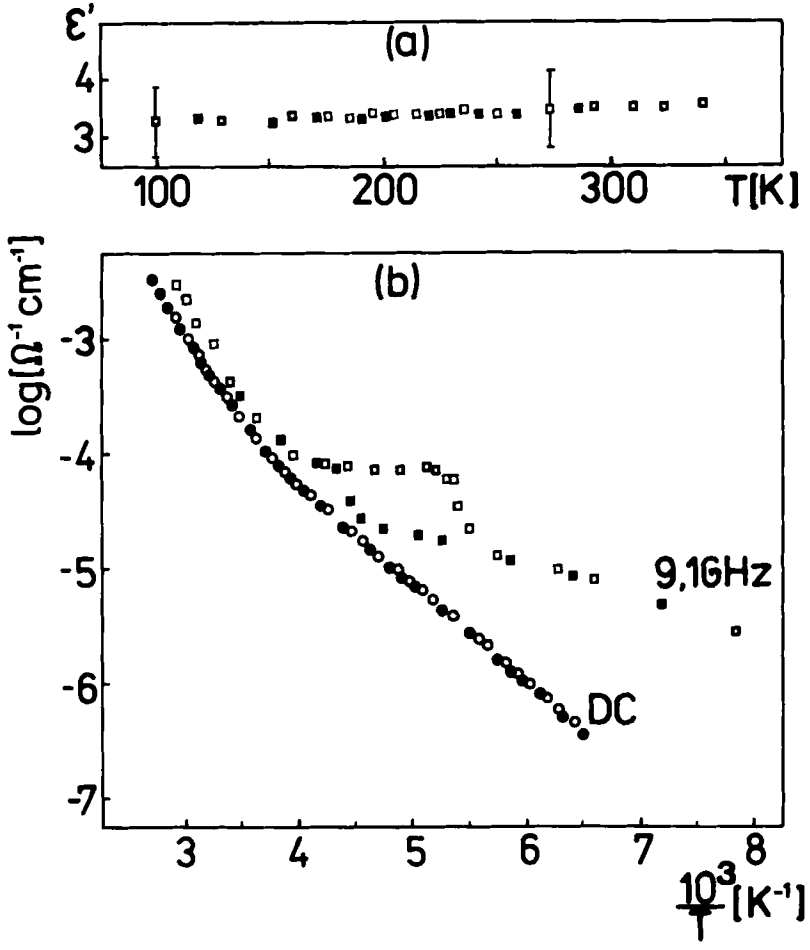


FIGURE 5 The electric permittivity ϵ' and the microwave conductivity σ_m for NMe2,4MePy(TCNQ)$_2$ along the a axis; the d.c. conductivity is also shown for comparison (open symbols for cooling run, full symbols for heating run).

tibility of NMe2,4MePy(TCNQ)$_2$ can be described by a 2-Dimensional Heisenberg system, in which the exchange integral is temperature dependent. We assume, of course, that the electron spin is localised on the TCNQ diad. This model is strongly supported by the present studies: we have shown the presence of only slightly-interacting diads of TCNQ, as well as the thermal contraction of the diad separations. The investigated temperature-dependence of the magnetic

susceptibility does not indicate any anomalies which could be interpreted as phase transition with hysteresis of magnetic susceptibility.

DISCUSSION

The intermediate value of the d.c. room-temperature conductivity ($\sigma_{RT} = 3.5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$) as well as the rather large gap (E_g = 0.66 eV) are consistent with the structural investigation which reveals the occurrence of segregated TCNQ diads. There is a poor overlap between TCNQ diads and for this reason the odd π electrons must be localised on each diad, and electron transfer between diads does not readily occur.

At low temperature the molecular ordering is essentially the same as that determined at room temperature; we observed small contractions of the order of 1% of intra- and inter-diad separations. These contractions, which are linear with temperature, do not explain the temperature behaviour of conductivity and the thermoelectric power in NMe2,4MePy(TCNQ)$_2$. In addition to the contraction, the cation has a tendency to draw towards the equilibrium position at the centre of symmetry. The disorder of the cations may provide a possible clue to the temperature dependence of the electrical conductivity.

It seems that the best explanation of the temperature behavior of d.c. conductivity as well as the thermoelectric power in NMe2, 4MePy(TCNQ)$_2$ is provided by the model based on the one-electron approximation with deep lying localised impurity states, influencing conduction at low temperatures by their thermal ionisation. This model has been used by us[11] for TCNQ salts with symmetrically substituted methyl-pyridinium cations. The main assumptions of our model were drawn from the following experimental data: 1) the strong negative temperature-dependence of thermoelectric power (thus ruling out hopping as a dominant transport mechanism) and 2) the existence of an activation energy of conductivity appreciably smaller at low temperatures than at higher ones.

The last fact indicates the presence of deep-lying donor impurities governing carrier concentration in the "extrinsic range". The conductivity in the extrinsic range can be expressed by,

$$\sigma_{ex} = en\mu_e$$

where μ_e is the electron mobility and n is the carrier concentration.

If the temperature is high enough to excite an electron from the valence to the conduction band, the concentration of holes p becomes comparable with the concentration of electrons n, and the conductivity starts to be "intrinsic" described by,

$$\sigma_i = en_i(\mu_e + \mu_n)$$

where μ_n is the hole mobility and n_i is the intrinsic pair density.

Between these two ranges, a transition region exists for which the Fermi level moves down towards the middle of the gap and the impurities tend to be exhausted.

Using the arguments presented previously[11] for TCNQ complex salts with symmetrically methyl substituted pyridinium cations we can calculate the temperature-dependence of the electron (n_e) and hole (n_h) concentrations in the conduction band as well as the intrinsic pair density n_i. These values are shown in Figure 6. It is apparent that for the low temperature region the hole concentration n_h is small in comparison with n_e and can be neglected in the calculation of the d.c. conductivity σ_{dc} and the Seebeck coefficient S, for $N_d > N_a$. For the salts under discussion this occurs for temperatures below 250 K approximately. It can also be seen, that n_e and n_h are the same as n_i for temperatures above about 300 K.

The temperature-dependence of the Fermi level E_F calculated as before[11] is shown in Figure 7. The Fermi level, in the extrinsic range, increases as the temperature decreases; this change depends on the degree of impurity compensation. At high temperature, about 300 K the Fermi level approaches the centre of the gap and the conductivity becomes intrinsic.

In the computer analysis, the best fit to both conductivity and Seebeck data was obtained when the mobility ratio, $c = \mu_e/\mu_h$, was dependent on temperature,

$$c = \mu_e/\mu_h \propto T^{-0.38}$$

This result is not inconsistent with band theory.

The line in Figure 3 shows the best fit of the Seebeck coefficient, consistent with the conductivity data, in accordance with equations:

$$S = -\frac{k}{e}\frac{(c-1)}{(c+1)}\left(\frac{E_g}{2kT} + 2\right)$$

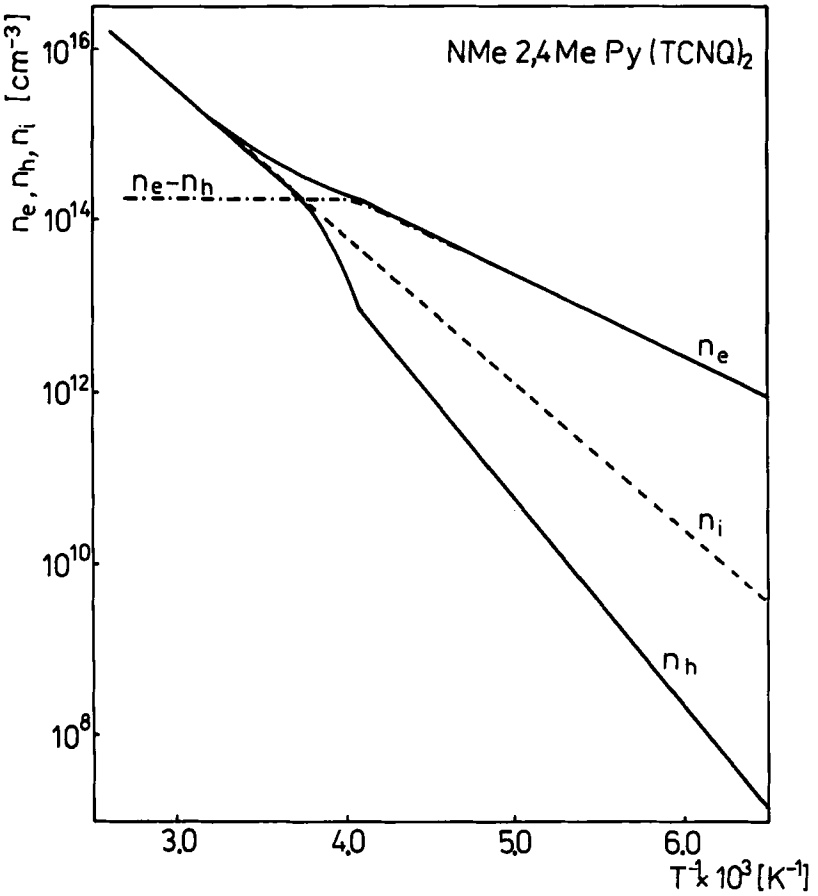


FIGURE 6 Temperature-dependence of electron (n_e) and hole (n_h) concentrations and the intrinsic pair density (n_i) calculated for NMe2,4MePy(TCNQ)$_2$. The difference ($n_e - n_h$) is also shown.

for the intrinsic range, and

$$S = -\frac{k}{e}\left(2 + \frac{E_C - E_F}{kT}\right)$$

for the extrinsic range.[11]

The line in Figure 2 is the best fit to equations for partially compensated 1-*D* semiconductor models (see also [11]).

All the parameters used for fitting the conductivity and thermopower data of NMe2,4MePy(TCNQ)$_2$ to the model based on the one-electron approximation with deep lying localised impurity states

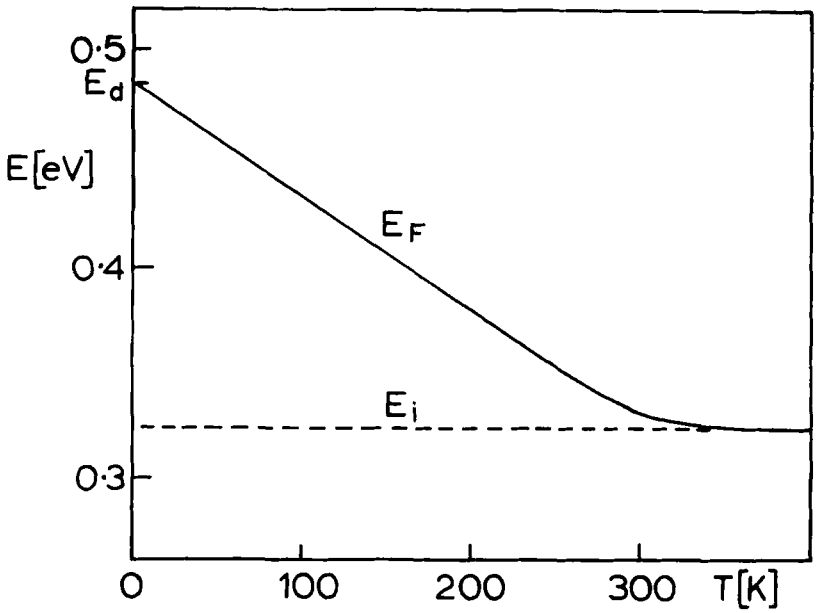


FIGURE 7 The Fermi level E_f vs. temperature calculated for NMe2,4MePy(TCNQ)$_2$. The donor level energy E_d, and Fermi level in the intrinsic range, E_i, are also shown.

are shown below:

$$|N_d - N_a| = 1.7 \times 10^{14}\ \text{cm}^{-3}, \qquad \mu_e \propto T^{-0.73}, \qquad \mu_n \propto T^{-0.35}$$

$$\mu(300\ \text{K}) = 1.3\ \text{cm}^2/\text{V s}, \qquad N_d = 3.25 \times 10^{16}\ \text{cm}^{-3},$$

$$Y N_a = 3.23 \times 10^{16}\ \text{cm}^{-3}, \qquad E_j = 0.17\ \text{eV}, \qquad E_g = 0.66\ \text{eV}.$$

The calculated values of electrically active impurity concentrations, N_d and N_a, lie about 10^{16} cm^{-3}, making less than 0.01% of the total content of TCNQ in the crystal. The small value obtained for $(N_d - N_a)/N_a$ means that the compensation is quite high and confirms the reasonableness of the model applied; also the mobility value about 1.3 cm^2/V s at room temperature is sufficiently large to apply band theory to the transport properties in NMe2,4MePy (TCNQ)$_2$.

Neither the temperature variations of the crystal structure nor the d.c. conductivity measurements on single, needle-shaped, crystals show any anomaly indicative of a phase transition. The same conclusion can be drawn from static magnetic susceptibility, IR absorption, and also

electric permittivity measurements performed on a mixture of single crystals and the larger irregular form which may not consist of single crystals. All these properties are reversible without hysteresis.

This evidence indicates that the thermal anomaly of the microwave conductivity σ_m,[13] shown also in Figure 5b, which is similar to the anomalies of d.c. conductivity observed by Yoshimura and Murakami[4] and by Shirotani *et al.*[10] for N-alkyl-substituted pyridinium is not caused by a structural phase transition.

Several interpretations of the microwave conductivity are possible, one of which has been mentioned previously.[13] We have suggested that the differences in the morphology of the crystals and consequently the differences in the surface to volume ratios could be responsible for the observed anomaly. The surfaces of microdomains of large, irregular crystals may influence the microwave conductivity as "capacitance elements" and cause the anomaly.

Another possible explanation for the anomaly could relate to the thermodynamic size effect of small dielectric particles observed by Rappaz *et al.*[19] Assuming a polycrystalline structure for our large and irregular product we can expect a contraction in the crystal lattice whose magnitude decreases with increasing particle size, leading to a multi-twinned structure, with non uniform strains and structural defects, since the surface planes are more distorted than the interior. Hence, the structure of polycrystals must be somewhat different from that of single crystals, and may well have distinctive electrical properties.

A third possible explanation for the observed anomaly follows from our structural investigation at low temperature. It is probable that the shift of the cation centre from the centre of symmetry, which is larger at room temperature than at low temperature, is not energetically favourable. This would be consistent with the observed tendency of the cation to draw towards the equilibrium position at the centre of symmetry as the temperature is lowered. It is possible that this movement is nonlinear with temperature and is different for temperatures decreasing and increasing. If so, it could be related to the a.c. conductivity anomaly.

The comparison of present results for NMe2,4MePy$(TCNQ)_2$ with the results for symmetrically-substituted (i.e. NMe2, 6MePy$(TCNQ)_2$ and NMe3, 5MePY $(TCNQ)_2$) shows a small influence of the position of the substitution for *N*-methyl-substituted pyridinium salts. It seems that the size of the *N*-alkyl-substituent plays a more important role than the positions of the ring substituents.

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