Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Electrical Properties and Structures of N-Methylcinnaline TCNQ Complexes

Zhu Daoben [a] , Wang Ping [a] , Qian Minwie [a] & Qian Renyuan [a]
[a] Institute of Chemistry, Academia Sinica, China
Version of record first published: 20 Apr 2011.

To cite this article: Zhu Daoben , Wang Ping , Qian Minwie & Qian Renyuan (1985): Electrical Properties and Structures of N-Methylcinnaline TCNQ Complexes, Molecular Crystals and Liquid Crystals, 128:3-4, 321-327

To link to this article: http://dx.doi.org/10.1080/00268948508079499

Mol. Cryst. Liq. Cryst., 1985, Vol. 128, pp. 321–327
0026-8941/85/1284–0321/$15.00/0

Printed in the United States of America

Electrical Properties and Structures of N-Methylcinnaline TCNQ Complexes

ZHU DAOBEN, WANG PING, QIAN MINWIE and QIAN RENYUAN

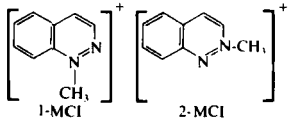
Institute of Chemistry, Academia Sinica, China

(*Received January 8, 1985*)

The new charge transfer complexes of 1-methylcinnaline $(TCNQ)_2$ [1-MCI $(TCNQ)_2$] and 2-methylcinnaline $(TCNQ)_2$ [2-MCI $(TCNQ)_2$] have been synthesized and characterized by elemental analysis, spectrum, X-ray diffraction and d.c. conductivity. The both complexes posses a triclinic unit cell and 1-d. stacking of TCNQ molecules but their distance between TCNQ molecules and overlap of TCNQ molecules in TCNQ column are quite different. The d.c. conductivity alonga-axis of 1-MCI $(TCNQ)_2$ and 2-MCI $(TCNQ)_2$ are 20 $(\Omega\ cm)^{-1}$ and 10^{-3} $(\Omega cm)^{-1}$ respectively. 1-MCI $(TCNQ)_2$ presents a "metal" like character above 327 k and a semiconductivity character below.

INTRODUCTION

One-dimensional tetracyano-p-quinodimethane (TCNQ) complexes have been extensively studied in the past decade because of a variety of electronic and magnetic properties and the phase transition due peierls instability of the one dimensional system.[1] The solid-state properties of TCNQ complexes depend essentially on the cation structure. In spite of extensive recent work, it is still difficult to specify cation structure requirements for high conductivity TCNQ complexes. Pyridazine and compounds containing pyridazine structures as donors have been of interest in the synthesis of low dimensional conductors.[2] We have recently synthesized new TCNQ charge transfer complexes of 1-MCI $(TCNQ)_2$ and 2-MCI $(TCNQ)_2$. The molecular structures of these cations are as follows



1-MCI 2-MCI

In this paper the synthesis, structure characterization and electrical properties of these methyl cinnaline TCNQ complexes are described.

EXPERIMENTAL

MCI $(TCNQ)_2$ were synthesized using the method Melby et. al.[3] N-methyl-cinnalinium iodides were obtained by the reaction of cinnaline and methyliodide, two isomers, i.e. 1N-methyl-cinnalinium iodide and 2N-methyl-cinnalinium iodide were not isolated. MCI $(TCNQ)_2$ complexes were prepared by the following procedure: 1 mMOL of N-methyl-cinnalinium iodides was dissolved in acetonitrile and heated under nitrogen atmosphere, 2 mMOL of TCNQ in acetonitrile was added and the solution was heated for 0.5 h. Black plate-shaped crystals with metallic lustre were separated out on cooling solution for a day. After slowly evaporating the residual solvent for several days black needle shaped crystals with metallic lustre were taken off. Both forms of the crystals have 1:2 stoichiometry as confirmed by elemental analysis and UV-VIS and IR spectra. Cell parameters were obtained by least square refinement of θ values of 25 high angle ($2\theta > 30°$) reflections. Intensities data collected on NICOLET P3/R3 diffractometer with graphite monochromated Mokα radiation in the $\omega/2\theta$ scanning mode. Structure was solved by direct methods with the SHELXYL program on ECLIPSE S140 computer followed by fourier techniques and was refined by means of block least square for a scale factor, positional and anisotropic thermal parameters. The final $R = 0.0537$ (1230 independent reflections) and 0.0474 (1736 independent reflections) for needle-shaped crystal and plate-shaped crystal respectively.

RESULTS AND DISCUSSION

X-ray diffraction studies have shown that both forms of the crystals have triclinic structure and P 1 space group. The unite cell parameters of the needle shaped crystal which was found to be 1-MCI $(TCNQ)_2$ are a = 6.515 (70) A, b = 7.715 (30) A, c = 13.914 (61) A, α = 88.39 (40), β = 84.28 (80), γ = 78.74 (9) and those of the plate shaped crystal which was found to be 2-MCI $(TCNQ)_2$ are a = 7.570 (10) A, b = 7.598 (70) A, c = 13.032 (74) A, α = 86.92 (30), β = 80.92 (10), γ = 69.39 (30). The molecular packings of 1-M CI $(TCNQ)_2$ and 2-MCI $(TCNQ)_2$ in the crystals are shown in Figure 1. Both

structures showed segregated columns of TCNQ anions and MCI cations. The TCNQ stacking in 1-MCI $(TCNQ)_2$ contains diads with an interdiad distance of 3.269 A and intradiad distance of 3.244A, the difference between them, 0.025 A, is very small. The overlapping mode is of the ring-exocyclic double-bond type as observed in other highly conducting TCNQ complexes. However the TCNQ stacking in 2-MCI $(TCNQ)_2$ showing a quite different packing, 2-MCI $(TCNQ)_2$ contains diad (TCNQ A and TCNQ B) with an intradiad distance of 3.212 A and their overlapping modes are the ring-exocyclic double-band but there is slightly overlap between TCNQ(B) and TCNQ(A′) through terminal $C(CN)_2$ groups with an interplanar distance of 3.312

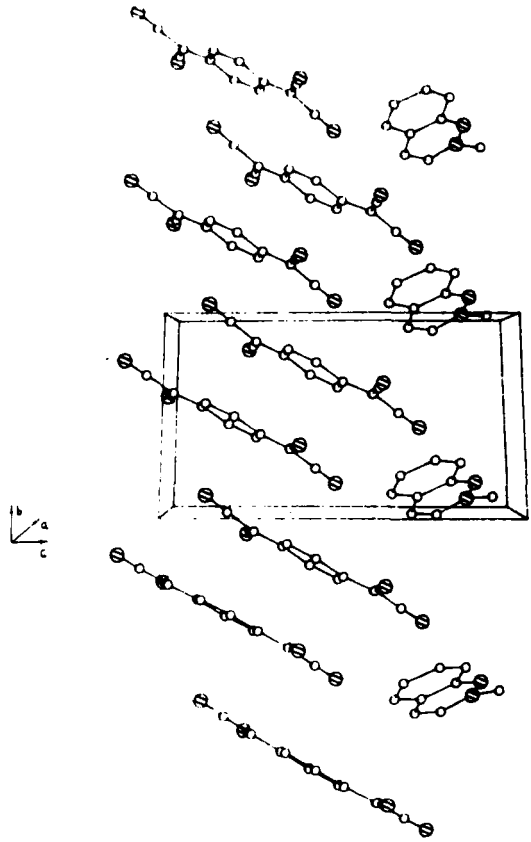


FIGURE 1 (a) The stacking of molecules in 2-MCI $(TCNQ)_2$ crystal along (100). (b) The numbering of atoms in TCNQs, the overlap between neighbouring TCNQs and the stacking of molecules 1-MCI $(TCNQ)_2$ crystal along (010).

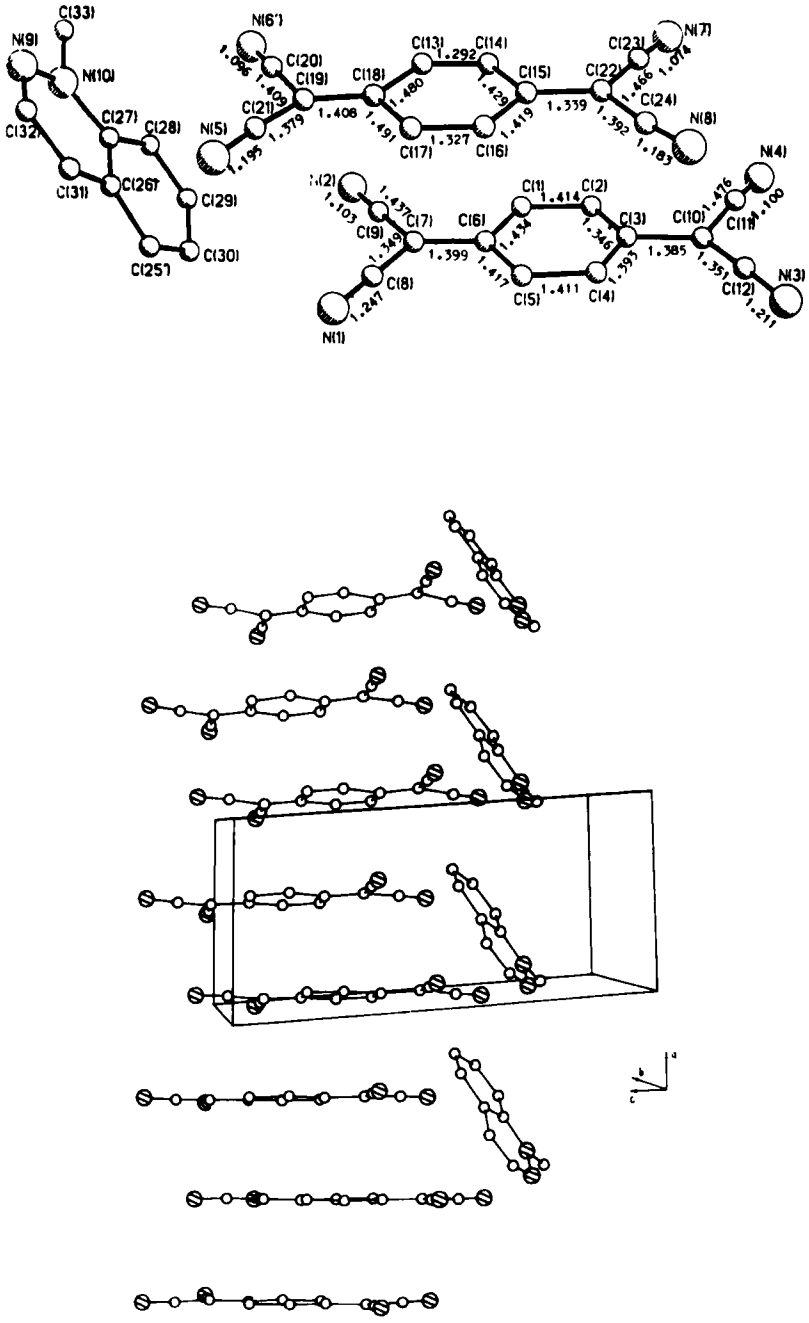


FIGURE 1 (continued)

A. These stacking are considered to be important for the electrical conducting phenomena as will be described later.

It has been suggested that the bond lengths in TCNQ molecules, particularly the bond lengths b and c, are sensitive to the extent of charge transfer and have been used to determine the apparent charge on the TCNQ molecule.[4] The mean bond lengths of chemically equivalent bonds of TCNQ molecules in 2-MCI $(TCNQ)_2$ are summarized in Table 1.

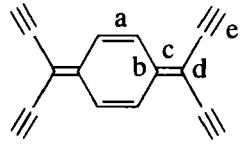


TABLE I

Mean bond lengths of the TCNQ molecules in 2-MCI $(TCNQ)_2$

	a	b	c	d	e
2-MCI $(TCNQ)_2$	A 1.345 (6),	1.420(4),	1.404(4),	1.403(10),	1.145(4)
	B 1.344(5),	1.439(4),	1.392(5),	1.414(5),	1.150(4)
$TCNQ^{-1}$	1.360(11),	1.422(10),	1.420(5),	1.418(7),	1.143(5)
TCNQ	1.344(4),	1.442(3),	1.373(4),	1.435(3),	1.138(3)

The mean bond lengths of TCNQ(A) and TCNQ(B) of 2-MCI $(TCNQ)_2$ are roughly identical. This suggests that unit negative charge is delocalized with $-1/2$ charge on each TCNQ molecule. It is interesting to observe that the bond lengths of TCNQ(A) and (B) of 1-MCI $(TCNQ)_2$ are strongly deviated from those in neutral and radical anion species in other complexes as shown in Figure 1b.

The room temperature specific conductivity along the needle axis of the crystals of 1-MCI $(TCNQ)_2$ were found to be 10–20 $(\Omega\ cm)^{-1}$. The temperature dependance of the conductivity, σ (T)/σ (RT), exhibited metallic behaviour at temperatures above 327 K as shown in Figure 2. At low temperatures a discontinuity in conductivity was observed at 245 K. The value of conductivity drop was found to be not reproducible over two more cycles on a given sample. The room temperature conductivity values observed along a,b and c of crystals of 2-MCI $(TCNQ)_2$ were 9×10^{-3}, 1.6×10^{-3} and 1.3×10^{-3} $(\Omega\ cm)^{-1}$ respectively using Montgomery's method. The temperature dependence of conductivity is showing in Figure 3. The aniostropy of conductivity decreases with decreasing temperature.

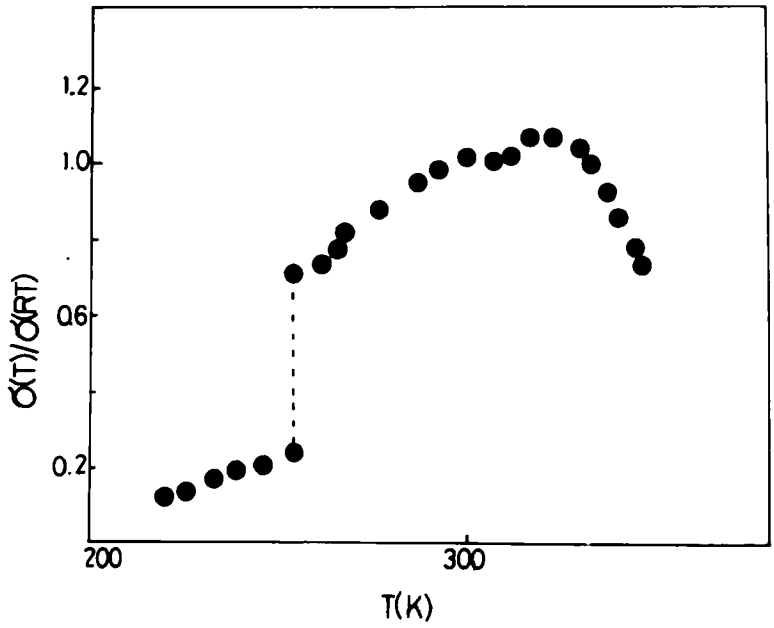


FIGURE 2 The temperature dependence of the conductivity of 1-MC-$(TCNQ)_2$.

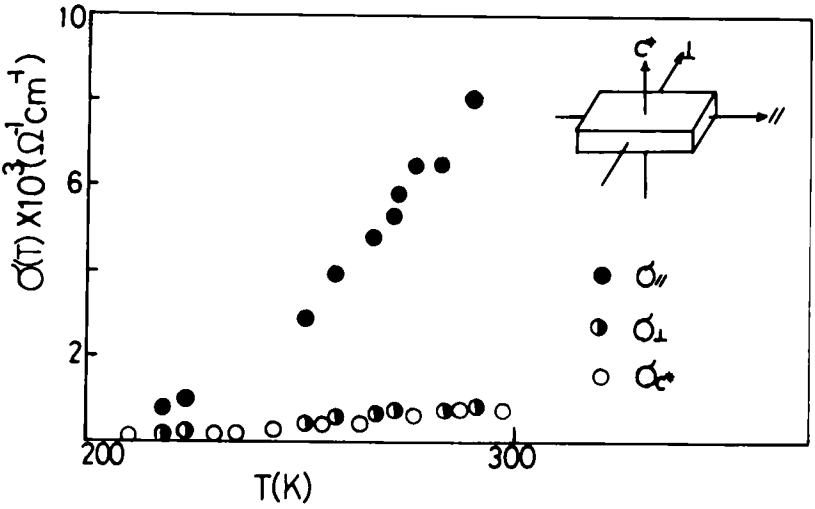


FIGURE 3 The anisotropy of conductivity of 2-MCI $(TCNQ)_2$.

References

1. B. Torrance, *Acc. Chem Res.*, **12**, 79 (1979).
2. A. Jchel et.al. *Synthetic Metals*, **6**, 258 (1983).
3. R. Melby et.al. *J. Am. Chem. Soc.*, **84**, 3374 (1962).
4. M. Konno and Y. Saito, *Acta Cryst.*, B**37**, 2034 (1981).