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The Crystal Structure of the Semiconducting Form of *N*-Methylphenazinium 7,7,8,8-Tetracyanoquinodimethanide*

By B. Morosin

Sandia Laboratories, Albuquerque, New Mexico 87115, *U.S.A.*

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The semiconducting form of *N*-methylphenazinium 7,7,8,8-tetracyanoquinodimethanide, usually known as NMP–TCNQ(II), crystallizes in space group $P2_1/n$ with $a=10{\cdot}558$ (5), $b=25{\cdot}952$ (4), $c=7{\cdot}0872$ (9) Å, $\beta=90{\cdot}68$ (1)° and $Z=4$. The ions alternate in columns parallel to the c axis with slightly unequal interplanar spacing, suggesting a possible pairing of the ions. Interatomic separations of the TCNQ ion suggest this species is probably of charge (−1).

Introduction

The physical properties of the highly conducting charge transfer salts of 7,7,8,8-tetracyanoquinodimethanide, usually denoted as TCNQ, have been intensively studied in recent years (Garito & Heeger, 1974; Soos, 1974). Several of these salts show very high one-dimensional room-temperature electrical conductivity. Of particular importance is one of the first such organic 'metals' studied, that formed with the *N*-methylphenazinium ion, usually denoted as NMP. This 1:1 charge transfer compound has been shown to form two crystallographically different phases, a highly conducting triclinic phase (Fritchie, 1966) and a semiconducting monoclinic phase (Coleman, Khanna, Garito, Heeger & Morosin, 1972; hereinafter CKGHM), which have been designated as NMP–TCNQ(I) and NMP–TCNQ(II), respectively. The crystal structure determination of NMP–TCNQ(II) is reported in this communication.

Experimental details

The growth of NMP–TCNQ(II) crystals has been reported previously by CKGHM. These crystals are laths, elongated along **c**, which appear deep violet upon reflection and, hence, are easily distinguishable from the physically similar, but black, NMP–TCNQ(I) triclinic form. The crystals were kindly supplied by Professor A. J. Heeger, University of Pennsylvania. Precession and Weissenberg photographs were consistent with systematic absences $h+l$ odd for $h0l$ and k odd for $0k0$, suggesting space group $P2_1/n$. Lattice parameters determined on a Picker diffractometer with Cu $K\alpha$ radiation (λ for $K\alpha_1=1{\cdot}54050$ Å) were $a=10{\cdot}558$ (5), $b=25{\cdot}952$ (4), $c=7{\cdot}0872$ (9) Å and $\beta=90{\cdot}68$ (1)°. The Cu $K\alpha$ (Ni-filtered) intensity data were measured with a scintillation detector employing pulse-height discrimination; the θ–2θ scan technique (to 130° 2θ) was used with a scan speed of 1 deg min^{-1} over the interval $2\theta_{\lambda_1}-1{\cdot}325°$ to $2\theta_{\lambda_2}+1{\cdot}325°$. A complete hemisphere of measured intensities yielded 2087 observed and 1180 'less than' intensities. The 'less than' intensities were those in which the intensity value was less than 3σ, where $\sigma=[1/n\ .\ (N_{sc}+K^2N_B)]^{1/2}$ and N_{sc}, N_B, K and n are the total scan count, background counts, the time ratio of the scan to background and number of equivalent values, respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). The structure was determined by direct methods and refined by least-squares methods. The function $\sum w(F_o-F_c)^2$ was minimized with $w=1/\sigma^2$. A residual value, R, where $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0·15 was obtained using isotropic thermal parameters. From a difference Fourier synthesis, H positions were obtained for all but the methyl C, where the peaks appeared to be related to thermal motion rather than scattering from H positions. The H atoms were assigned the isotropic thermal parameters of the C atoms to which they are bonded and these H positions with fixed thermal parameters were subjected to further least-squares refinement. Values of R equal to 0·134 with isotropic thermal parameters and 0·067 with anisotropic parameters were obtained.† The final parameters are given in Table 1 using the labeling scheme shown in Fig. 1. The H atoms are labeled with the same number as the C atom to which they are bonded. No H atoms for the methyl group, C(35), were included in the refinement because of the large anisotropic thermal motion for C(35); however, reasonably well-defined density peaks at the appropriate locations of (0·840, 0·495, 0·000), (0·672, 0·475, −0·114) and (0·672, 0·488, 0·143) are found in the final difference synthesis calculated at the conclusion of the refinement. The corresponding interatomic separations and angles are given in Table 2. The computations were performed with the X-RAY 72 System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31345 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters for NMP–TCNQ*(II)

Thermal parameters are of the form exp $(-2\pi^2\sum\sum U_{ij}h_ih_ja_i^*a_j^*)$ in units of 10^{-3} Å^2.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·1226 (4)	0·1305 (2)	−0·0691 (5)	41 (2)	43 (2)	34 (2)	1 (2)	−10 (2)	−4 (2)
C(2)	0·1957 (4)	0·1764 (2)	−0·0731 (5)	41 (2)	42 (2)	37 (2)	4 (2)	−12 (2)	−2 (2)
C(3)	0·3207 (4)	0·1764 (2)	−0·0183 (5)	39 (2)	42 (2)	37 (2)	−1 (2)	−8 (2)	3 (2)
C(4)	0·3814 (4)	0·1300 (2)	0·0404 (5)	39 (2)	47 (2)	29 (2)	4 (2)	−7 (2)	−3 (2)
C(5)	0·3092 (4)	0·0840 (2)	0·0378 (5)	49 (2)	40 (2)	40 (2)	3 (2)	−10 (2)	1 (2)
C(6)	0·1845 (4)	0·0842 (2)	−0·0136 (5)	46 (2)	38 (2)	39 (2)	−2 (2)	−10 (2)	−2 (2)
C(7)	−0·0064 (4)	0·1303 (2)	−0·1193 (5)	40 (2)	47 (2)	40 (2)	1 (2)	−13 (2)	−8 (2)
C(8)	0·5078 (4)	0·1296 (2)	0·0999 (6)	41 (2)	47 (2)	42 (2)	4 (2)	−11 (2)	1 (2)
C(9)	−0·0778 (4)	0·0839 (2)	−0·1252 (6)	43 (2)	55 (2)	49 (3)	0 (2)	−15 (2)	−6 (2)
C(10)	−0·0713 (4)	0·1758 (2)	−0·1718 (6)	35 (2)	53 (2)	44 (3)	2 (2)	−15 (2)	−5 (2)
C(11)	0·5839 (4)	0·1747 (3)	0·1068 (6)	36 (2)	60 (3)	45 (3)	10 (2)	−15 (2)	5 (2)
C(12)	0·5705 (4)	0·0830 (2)	0·1493 (6)	42 (2)	64 (3)	47 (2)	3 (2)	−10 (2)	2 (2)
C(21)	0·6577 (4)	0·3345 (2)	−0·1090 (5)	40 (2)	45 (2)	31 (2)	−0 (2)	−10 (2)	6 (2)
C(22)	0·5604 (4)	0·3019 (4)	−0·1727 (6)	51 (3)	59 (3)	43 (3)	−10 (2)	−13 (2)	10 (2)
C(23)	0·4408 (4)	0·3217 (2)	−0·2007 (7)	39 (3)	85 (4)	48 (3)	−11 (3)	−12 (2)	18 (3)
C(24)	0·4178 (4)	0·3730 (2)	−0·1695 (7)	39 (3)	102 (4)	41 (3)	7 (3)	−6 (2)	15 (3)
C(25)	0·5130 (4)	0·4054 (2)	−0·1065 (7)	52 (3)	72 (3)	51 (3)	19 (3)	−9 (2)	4 (3)
C(26)	0·6350 (4)	0·3866 (2)	−0·0742 (6)	45 (2)	46 (3)	33 (2)	10 (3)	−10 (2)	2 (2)
C(28)	0·8515 (4)	0·3965 (2)	0·0325 (5)	45 (2)	46 (3)	32 (3)	−3 (3)	−12 (2)	6 (2)
C(29)	0·9496 (4)	0·4257 (2)	0·1140 (6)	59 (2)	63 (2)	44 (2)	−15 (3)	−17 (2)	3 (2)
C(30)	1·0653 (5)	0·4027 (2)	0·1510 (6)	51 (3)	97 (4)	40 (3)	−21 (3)	−14 (2)	−1 (3)
C(31)	1·0862 (5)	0·3512 (2)	0·1120 (7)	39 (3)	104 (3)	46 (3)	4 (2)	−13 (2)	2 (3)
C(32)	0·9902 (4)	0·3217 (2)	0·0355 (6)	43 (3)	73 (3)	41 (2)	10 (2)	−14 (2)	−0 (2)
C(33)	0·8734 (4)	0·3446 (2)	−0·0048 (9)	41 (2)	50 (3)	31 (2)	−0 (2)	−10 (2)	3 (2)
C(35)	0·7114 (6)	0·4735 (2)	0·0132 (9)	119 (5)	38 (3)	101 (5)	18 (3)	−55 (4)	−11 (3)
N(13)	−0·1314 (4)	0·0457 (2)	−0·1326 (7)	75 (3)	65 (3)	86 (3)	−20 (3)	−27 (3)	−9 (2)
N(14)	−0·1244 (4)	0·2129 (2)	−0·2125 (6)	48 (3)	61 (2)	67 (3)	8 (3)	−19 (2)	−1 (2)
N(15)	0·6462 (4)	0·2110 (2)	0·1148 (6)	46 (3)	65 (2)	75 (3)	−8 (3)	−18 (2)	8 (2)
N(16)	0·6201 (4)	0·0448 (2)	0·1872 (7)	66 (3)	73 (3)	88 (3)	25 (2)	−12 (3)	22 (3)
N(27)	0·7344 (4)	0·4175 (1)	−0·0126 (5)	58 (2)	37 (2)	44 (2)	6 (2)	−21 (2)	−9 (2)
N(34)	0·7771 (3)	0·3149 (1)	−0·0834 (5)	39 (2)	45 (2)	40 (2)	4 (2)	−15 (2)	1 (2)

Table 1 (*cont.*)

	x	y	z	$u(\times 10^4)$
H(6)	0·127 (5)	0·059 (2)	−0·010 (7)	443
H(5)	0·355 (5)	0·052 (2)	0·075 (7)	456
H(3)	0·374 (4)	0·216 (2)	−0·018 (7)	418
H(2)	0·152 (5)	0·210 (2)	−0·122 (7)	431
H(22)	0·582 (5)	0·265 (2)	−0·195 (7)	532
H(23)	0·376 (5)	0·294 (2)	−0·244 (7)	608
H(24)	0·321 (5)	0·384 (2)	−0·167 (8)	709
H(25)	0·506 (5)	0·448 (2)	−0·094 (8)	633
H(29)	0·933 (5)	0·466 (2)	0·125 (8)	608
H(30)	1·136 (5)	0·423 (2)	0·212 (8)	659
H(31)	1·711 (6)	0·337 (2)	0·132 (8)	697
H(32)	0·997 (6)	0·285 (2)	−0·000 (8)	570

Discussion

As suggested by the very different physical properties of NMP–TCNQ(II) compared with its other phase, NMP–TCNQ(I), the overall molecular packing is also dissimilar (CKGHM). In this phase, the ions alternate in columns parallel to the *c* axis (Fig. 1). Furthermore, within such a column, the spacing of an NMP ion below or above the TCNQ ion is not identical, suggesting a 'pairing' of the two ions. For example, from the stacking sequence shown in Fig. 1(*b*), there are five nearest contacts equal to or less than 3·5 Å between atoms of the labeled NMP ion to the unlabeled (lower) TCNQ ion (range 3·35–3·50 Å) while there are 16 such contacts to the labeled (upper) TCNQ ion (range 3·13–3·49 Å) of which 13 are shorter than the shortest (3·35 Å) value for an NMP–TCNQ (lower) distance. Least-squares planes through the main skeleton of the ions [*i.e.* through C(1)–C(8) for TCNQ and all but H

Table 2. *Bond lengths and angles*

(*a*) TCNQ

C(1)—C(2)	1·421 (6) Å	C(6)—C(1)—C(2)	117·8 (3)°
C(1)—C(6)	1·420 (6)	C(5)—C(4)—C(3)	118·0 (3)
C(3)—C(4)	1·424 (6)		
C(5)—C(4)	1·416 (6)	C(2)—C(1)—C(7)	121·5 (4)
		C(6)—C(1)—C(7)	120·7 (4)
C(1)—C(7)	1·404 (5)	C(3)—C(4)—C(8)	121·3 (4)
C(4)—C(8)	1·395 (5)	C(5)—C(4)—C(8)	120·7 (4)
C(2)—C(3)	1·372 (5)	C(1)—C(2)—C(3)	120·9 (4)
C(5)—C(6)	1·361 (6)	C(1)—C(6)—C(5)	121·2 (4)
		C(4)—C(5)—C(6)	121·2 (4)
C(7)—C(9)	1·421 (6)	C(4)—C(3)—C(2)	120·8 (4)
C(7)—C(10)	1·413 (6)		
C(8)—C(11)	1·420 (6)	C(1)—C(7)—C(9)	121·5 (4)
C(8)—C(12)	1·420 (6)	C(1)—C(7)—C(10)	122·0 (4)
		C(4)—C(8)—C(11)	123·0 (4)
C(2)—H(2)	1·03 (5)	C(4)—C(8)—C(12)	121·4 (4)
C(3)—H(3)	1·06 (5)		
C(5)—H(5)	1·04 (5)	C(9)—C(7)—C(10)	116·4 (4)
C(6)—H(6)	1·04 (5)	C(11)–C(8)—C(12)	115·5 (4)
C(9)—N(13)	1·142 (6)	C(7)—C(9)—N(13)	177·5 (5)
C(10)–N(14)	1·148 (6)	C(7)—C(10)–N(14)	179·3 (4)
C(11)–N(15)	1·150 (6)	C(8)—C(11)–N(15)	179·1 (5)
C(12)–N(16)	1·152 (7)	C(8)—C(12)–N(16)	178·9 (5)

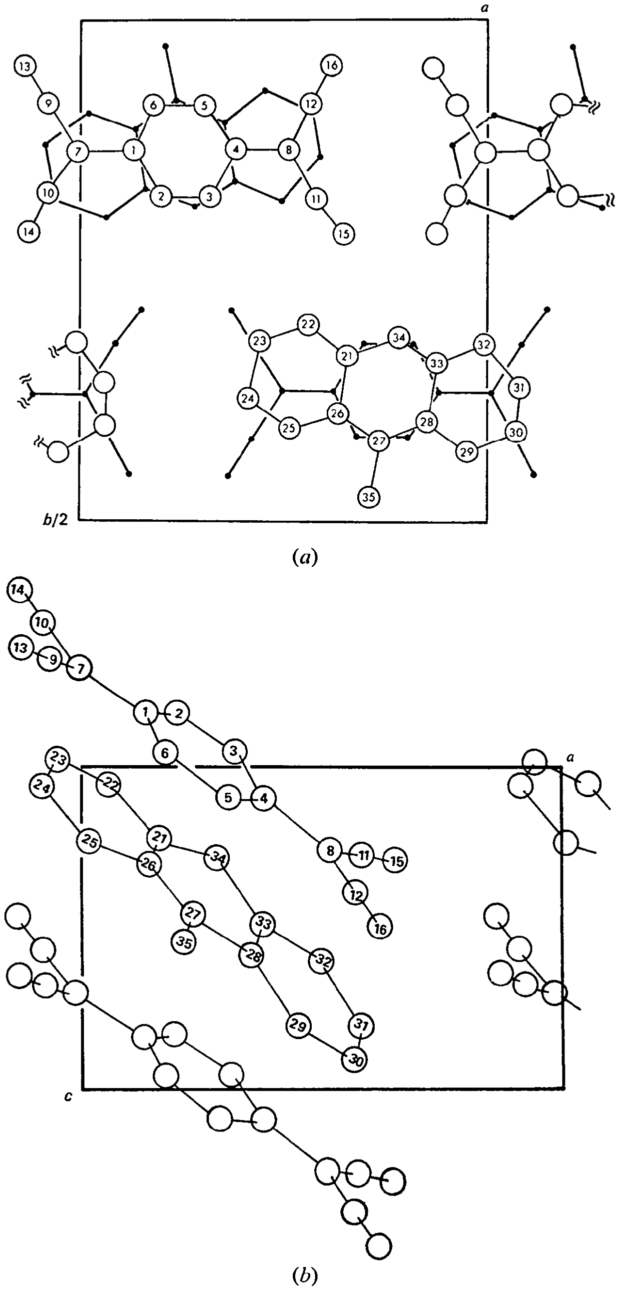
Table 2 (*cont.*)

(*b*) NMP

N(34)–C(21)	1·370 (5)	N(34)–C(21)–C(26)	119·8 (4)
N(34)–C(33)	1·388 (5)	N(34)–C(33)–C(28)	119·4 (4)
C(21)–C(22)	1·402 (6)	N(27)–C(26)–C(21)	119·0 (4)
C(33)–C(32)	1·395 (6)	N(27)–C(28)–C(33)	119·1 (4)
C(25)–C(26)	1·394 (6)	N(34)–C(21)–C(22)	119·2 (4)
C(28)–C(29)	1·404 (6)	N(34)–C(33)–C(32)	119·2 (4)
C(21)–C(26)	1·394 (6)	N(27)–C(26)–C(25)	122·9 (4)
C(33)–C(28)	1·392 (6)	N(27)–C(28)–C(29)	122·3 (4)
C(23)–C(24)	1·372 (9)	C(22)–C(21)–C(26)	121·1 (4)
C(30)–C(31)	1·383 (8)	C(32)–C(33)–C(28)	121·4 (4)
C(22)–C(23)	1·376 (6)	C(21)–C(22)–C(23)	119·2 (4)
C(24)–C(25)	1·381 (7)	C(24)–C(25)–C(26)	120·4 (5)
C(32)–C(31)	1·377 (7)	C(28)–C(29)–C(30)	119·4 (5)
C(29)–C(30)	1·382 (7)	C(31)–C(32)–C(33)	119·3 (5)
C(26)–N(27)	1·388 (6)	C(22)–C(23)–C(24)	120·3 (5)
C(28)–N(27)	1·384 (6)	C(23)–C(24)–C(25)	120·9 (5)
		C(29)–C(30)–C(31)	121·5 (5)
C(35)–N(27)	1·487 (6)	C(30)–C(31)–C(32)	119·9 (5)
C(22)–H(22)	0·99 (5)	C(21)–C(26)–C(25)	118·2 (4)
C(23)–H(23)	1·04 (5)	C(33)–C(28)–C(29)	118·5 (4)
C(24)–H(24)	1·06 (6)		
C(25)–H(25)	1·12 (6)	C(26)–N(27)–C(35)	118·7 (4)
C(29)–H(29)	1·07 (5)	C(28)–N(27)–C(35)	120·2 (4)
C(30)–H(30)	1·01 (6)		
C(31)–H(31)	0·98 (6)	C(26)–N(27)–C(28)	121·0 (3)
C(32)–H(32)	0·98 (6)	C(21)–N(34)–C(33)	121·0 (3)

and C(35) for NMP] suggest an interesting feature of these two ions; that is, they are both slightly bowed in the same direction within a column. In particular, the root-mean-square deviation of the atoms defining the plane of the NMP ion is reduced from 0·062 Å to 0·008 and 0·010 Å if two planes meeting at the N atoms in the middle of the ion are used. An angle of 5·6° is formed between these two planes. (The ion is thus of C_s rather than C_{2v} symmetry.) Table 3 gives the deviation of the atoms from such planes. One notes that the bowing of the TCNQ skeleton occurs at the C(2)–C(5) 'line', reducing the D_{2h} symmetry; however, because of the small rotations about the C(1)–C(7) and C(4)–C(8) bonds, the C–N groups involving the N(14) and N(15) atoms of the TCNQ ion depart from the least-squares plane on the same side [with N(13) and N(16) on the opposite side] in what could be considered a *cis* (C_s symmetry) rather than *trans* (C_i symmetry) configuration. Such separations are consistent with the shorter contact separations between the ions. The separations smaller than 3·4 Å involving contacts between the columns include N(34)–N(14) at 2·992 (5), N(16)–C(35) at 3·317 (8), N(15)–N(14) at 3·374 (6) and N(13)–C(35) at 3·383 (8) Å.

The interatomic separations within the TCNQ ion (Table 2) are close to previously observed values in these compounds; in particular, one is able to suggest that the ion is negatively charged with a full electron by comparing our values with those predicted for a partial charge or neutral TCNQ group (Table 4; Herbstein, 1971). Values for the NMP ion are internally consistent with similar positional interatomic separa-



(*a*)

(*b*)

Fig. 1. (*a*) View along the *c* axis of NMP–TCNQ(II). The labeling scheme employed in this communication is shown; N atoms are 13, 14, 15, 16, 27, and 34 with the remainder C atoms; H atoms are not shown and employ the same number as the carbon to which they are attached. (*b*) Partial view along the *b* axis of NMP–TCNQ(II). This projection includes atoms with *y* values between 0 and ¼; labeled atoms of the NMP ion are symmetry related to those shown in (*a*) and given in the text.

Table 3. *Distances from least-squares planes through ions*

	Plane 1		Plane 2		Plane 3	
Plane defined through these atoms	C(1)	0·003 Å	C(21)	0·007 Å	C(28)	0·003 Å
	C(2)	−0·023	C(22)	0·004	C(29)	0·016
	C(3)	−0·012	C(23)	0·006	C(30)	−0·002
	C(4)	−0·002	C(24)	−0·010	C(31)	−0·012
	C(5)	−0·023	C(25)	−0·006	C(32)	0·002
	C(6)	−0·012	C(26)	0·010	C(33)	0·003
	C(7)	0·033	N(27)	0·003	N(27)	−0·015
	C(8)	0·036	N(34)	−0·013	N(34)	0·005
	$\sigma=0·023$		$\sigma=0·008$		$\sigma=0·010$	
	C(9)	−0·015	C(35)	−0·076	C(35)	−0·111
	C(10)	0·073	H(22)	0·005	H(29)	−0·102
	C(11)	0·070	H(23)	0·035	H(30)	0·027
	C(12)	−0·025	H(24)	0·186	H(31)	−0·082
	N(13)	−0·086	H(25)	−0·138	H(32)	−0·030
	N(14)	0·120				
	N(15)	0·112				
	N(16)	−0·086				
	H(6)	0·032				
	H(5)	−0·056				
	H(3)	−0·007				
	H(2)	−0·079				

tions (values so grouped in Table 2) as well as being similar to previously observed values in NMP (Fritchie, 1966),* quinolinium (Kobayashi, Marumo & Saito, 1971), acridinium (Kobayashi, 1974), and neutral phenazine (Herbstein & Schmidt, 1955); there is a slight trend involving the lengths along the width of the NMP ion, *i.e.*, C(23)–C(24) and C(21)–C(26), which suggests that our values are somewhat smaller. The refined positions of the H atoms gave C–H separations which ranged from 0·99 to 1·12 Å for the two ions.

Table 4. *Average TCNQ interatomic separations*

Type	TCNQ°	$TCNQ^{1/2-}$	$TCNQ^{-}$	This study
C(2)–C(3)	1·344 Å	1·354 Å	1·356 Å	1·366 Å
C(1)–C(2)	1·446	1·434	1·425	1·420
C(1)–C(7)	1·371	1·396	1·401	1·400
C(7)–C(9)	1·434	1·428	1·417	1·419
C(9)–N(13)	1·14	1·17	1·15	1·148
C(1)–C(2)—C(3)	120·0°	121·1°	121·2°	121·0°
C(2)–C(1)—C(6)	118·0	117·9	117·4	117·9
C(9)–C(7)—C(10)	116·3	115·9	115·2	115·9
C(7)–C(9)—N(13)	179·0	178·5	178·6	178·7

The contribution of the anisotropic thermal parameters is significant as the *R* value was reduced by nearly one-half on their introduction in the least-squares refinement. The largest thermal motion is exhibited by the methyl carbon and this is primarily in the plane of the NMP ion.

These crystals exhibit a strong e.s.r. signal characteristic of the TCNQ radical ion (the NMP ion has no unpaired spin). The exchange-narrowed line width is about one order of magnitude larger than in the metallic form [NMP–TCNQ(I)], which is consistent with the difference in stacking in the two forms. Details of the e.s.r. results will be published elsewhere (Hughes & Morosin, 1976).

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* We have refined Mo $K\alpha$ data on NMP–TCNQ(I) for both noncentrosymmetric ($P1$) and centrosymmetric ($P\bar{1}$) models (Morosin, 1975) using anisotropic thermal parameters and fixed hydrogen coordinates to residual index values *R* of 0·0570 and 0·0595, respectively. The *R*-factor ratio of 1·043 is too small to reject the hypothesis that the centrosymmetric space group is the correct space group even at a 25% significance level (Hamilton, 1965). Parameter values are in good agreement with Fritchie's values and are included in material deposited with this paper.