The Structure of the Low-Temperature Modification of N,N-Dimethylmorpholinium Di-7,7,8,8-tetracyano-p-quinodimethanide; DMM(TCNQ)$_2$ (Iα) at 95 K

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Abstract

Monoclinic DMM(TCNQ)$_2$ (I), space group $P2_1/m$ at 294 K, has two low-temperature modifications, (Iα) and (Iβ). The crystal structure of (Iα) is described: $T = 95$ K, $C_6H_{14}NO^+.2C_{12}H_4N_4^{1/2-}$, monoclinic, $P2_1/c$, $a = 13.280$ (4), $b = 26.497$ (4), $c = 14.782$ (4) Å, $\beta = 92.35$ (3)°, $V = 5197$ Å^3, $Z = 8$, $M_r = 524.6$, $D_x = 1.341$ Mg m^{-3}, Mo$K\bar{\alpha}$, $\lambda = 0.71069$ Å, $\mu = 0.095$ mm^{-1}, $F(000) = 2184$, $wR(F) = 0.062$ for 12 232 independent reflections. At 294 K, the DMM molecules in (I) are randomly disordered, occupying two positions related by the mirror plane in the structure. At the phase transition from (I) to (Iα) at $T_c = 260$ K, this disorder disappears. The DMM ordering is accompanied by slight shifts of the TCNQ molecules, which change the TCNQ stacks from dimeric to octameric. The physical significance of the structural changes is discussed.

Introduction

The charge-transfer salts of the organic electron acceptor 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) with substituted morpholinium groups as donors have been studied because of the characteristic electronic properties associated with the presence of pseudo one-dimensional stacks of TCNQ molecules (van Bodegom, 1979; Huizinga, 1980; for a recent general introduction to organic conductors see, for example, Bryce & Murphy, 1984). Particularly interesting are the relations between their physical properties and the crystal packing. DMM(TCNQ)$_2$ (DMM = N,N-dimethylmorpholinium) is an excellent example since, with this donor, both a monoclinic (I) and a triclinic (II) crystal modification are known at room temperature, with markedly different structures and properties (Schwerdtfeger, Oostra, Visser & Sawatzky, 1981; Korving, Hymans, Brom, Oostra, Sawatzky & Kommandeur, 1983). Moreover, both modifications undergo structural changes when the temperature is lowered. At room temperature, crystals of (I) have been shown to contain stacks of dimers (Kamminga & van Bodegom, 1981). Differential scanning calorimetry (DSC) has shown heat effects at 272 and 260 K. The interpretation of the magnetic sus-

ceptibility agrees with the presence of stacks of tetramers at low temperatures (Schwerdtfeger et al., 1981). Determination of the crystal structure at 95 K has been undertaken to reveal the structural changes occurring at the phase transition(s).

In a forthcoming paper the room-temperature crystal structure and the incommensurately modulated low-temperature structure of triclinic DMM(TCNQ)$_2$ (II) will be described (Visser & de Boer, 1985).

Experimental

A crystal with regular dimensions (0.5–0.7 mm) was selected from the batch that Kamminga & van Bodegom (1981) obtained by slowly cooling a mixture of hot solutions of DMM iodide and TCNQ in acetonitrile. It should be noted that all physical and structural data of (I) known at present have been obtained from crystals selected from this batch. Numerous attempts to crystallize new batches of the monoclinic crystals (I) were unsuccessful and rendered only the triclinic crystals (II). It seems that the original batch was the result of an accidental and as yet unretrieved variation of the crystallization conditions.*

For preliminary rotation and Weissenberg photographs at low temperatures, the crystal was cooled by a stream of cold nitrogen gas. The exposures revealed the existence of two monoclinic low-temperature modifications, (Iα) and (Iβ). Reflection symmetry and systematic absences indicated space group $P2_1/c$ for both modifications. The relation between cell (I) at room temperature and cells (Iα) and (Iβ) at low temperatures is depicted in Fig. 1.

For the measurement of the intensities at low temperatures the crystal of (I) was cooled on an Enraf–Nonius CAD4F diffractometer equipped with a nitrogen gas flow device, based on the system described by de Boer (1970) and van Bolhuis (1971).

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* Experiments on doping with DMTM [N,N-dimethylthiomorpholinium], to obtain mixed crystals of composition DMM$_{1-x}$DMTM$_x$(TCNQ)$_2$, have yielded, however, for small values of x a mixture of the monoclinic and the triclinic modification.

Unfortunately, on cooling on the diffractometer, only modification (Iα) could be retrieved. In spite of repeated attempts with various cooling rates, modification (Iβ) was not obtained. It is not certain whether the two peaks in the DSC curve are due to transitions to the phases (Iα) and (Iβ), or whether the measured excess entropy describes a complicated second-order phase transition from (I) to (Iα), with different thermal regimes. The latter explanation agrees with the fact that the newly appearing low-temperature (Iα) reflections are, even at room temperature, anticipated by diffuse spots, which do not all become sharp at the same temperature. Further detailed thermodynamic and X-ray studies are required to obtain a better insight into the structural changes during the phase transition.

Crystal data and reflection intensities for modification (Iα) were collected at 95 K with Mo $K\bar{\alpha}$ radiation. Graphite crystal and 'beam flattener' (Helmholdt & Vos, 1977) were used to obtain homogeneous monochromatic primary beam. Cell dimensions were calculated from diffraction angles of 22 accurately centred reflections with $24 < \theta < 25°$. Crystal data are listed in Table 1. During data collection, three low-order reference reflections with mutually roughly orthogonal diffraction vectors H were measured at regular intervals. Initial data set (set 1) of 16 048 intensities for one quarter of reciprocal space was measured in ω-2θ scan mode up to $\theta_{max} = 30°$. Exceptionally high background intensities for some reflections with H approximately parallel to short b^* axis pointed to occurrence of overlap with neighbouring intensity profiles. 4910 reflections with both $k \geq 2h$ and $k \geq 2l$ and $\theta \leq 30°$ were remeasured by ω-θ scan with adjusted aperture width of $(1\cdot7 + 1\cdot25 \tan \theta)$ mm and constant azimuthal angle of 30° chosen to avoid overlap (set 2). For both data sets corrections were applied for fluctuations in reference intensities ($\pm1\cdot8\%$). Corrections for absorption were omitted. After scaling of set 2 to set 1, according to Hamilton, Rollett & Sparks (1965), weighted average intensities were calculated for common reflections with $\Delta I < 3\sigma(\Delta I)$, for remaining common reflections intensities of set 2 were used.

Fig. 1. Relation between the unit cells of the monoclinic modifications of DMM(TCNQ)$_2$. (I) is the high-temperature and (Iα) and (Iβ) are the low-temperature modifications.

Table 1. *Crystal data for DMM(TCNQ)$_2$*
$[(C_6H_{14}NO)(C_{12}H_4N_4)_2]$

	(Iα)	(Iβ)*	(I)†
Temperature (K)	95	~120	294
Space group	$P2_1/c$	$P2_1/c$	$P2_1/m$
a (Å)	13·280 (4)	7·73 (4)	7·792 (7)
b (Å)	26·497 (4)	26·50 (4)	26·814 (8)
c (Å)	14·782 (4)	14·78 (4)	7·594 (7)
β (°)	92·35 (3)	120·9 (3)	58·44 (6)
V (Å^3)	5197	2598	1352
M_r	524·6	524·6	524·6
$F(000)$	2184	1092	546
Z	8	4	2
μ(Mo $K\bar{\alpha}$) (mm^{-1})	0·095	0·095	0·091
D_x (Mg m^{-3})	1·341	1·34	1·289

* Estimated from Weissenberg photographs.
† From Kamminga & van Bodegom (1981).

Resulting data set of 15 128 independent reflections was corrected for Lorentz and polarization effects. 1423 reflections with $I(net) < 0$ were given zero weight. For remaining 13 705 reflections, standard deviation in $|F_o|$, $\sigma_c(F_o)$, is based on counting statistics and on error in attenuation-filter factor.

Refinement

The unit cell of DMM(TCNQ)$_2$ (Iα) contains four independent TCNQ and two independent DMM molecules. Initial coordinates of the non-hydrogen atoms of the TCNQ moieties were calculated by transforming the atomic coordinates of the 294 K structure (Kamminga & van Bodegom, 1981) according to Fig. 1. After isotropic least-squares refinement, the non-hydrogen part of the two DMM molecules could be constructed from the 16 highest peaks in a difference Fourier map. After blocked matrix anisotropic refinement, with one molecule per block, the positions of the hydrogen atoms were found in a difference map. In the final refinement cycles the H atoms were constrained at 1·08 Å from their respective C atoms and given isotropic thermal smearing; reflection weights $w = [\sigma_c^2(F_o) + E|F_o|^2]^{-1}$ were calculated, with $E = 0\cdot0007$ giving a minimal variation of $w\Delta^2 = w(|F_o| - |F_c|)^2$ with $|F_o|$; 7 low-order reflections with $(w\Delta^2)^{1/2} > 5$ and reflections with $|F_o| < 2\sigma_c(F_o)$ were not taken into account.

$R = 0\cdot051$, $wR = 0\cdot062$ and $S = 1\cdot55$ with 12 232 contributing reflections and 766 variables. The maximum and average Δ/σ in the final cycle were 0·09 and 0·01 respectively. The final difference Fourier map showed maxima up to 0·48 e Å^{-3} at bonds and minima down to $-0\cdot35$ e Å^{-3} at the centres of the TCNQ molecules. At positions remote from the molecules maxima up to 0·22 e Å^{-3} were found, which is approximately three times the estimated standard deviation $\sigma(\Delta\rho) = (1/V)(\sum m\Delta^2)^{1/2} = 0\cdot07$ e Å^{-3}, where m is the reflection multiplicity and the summation is over all reflections included in the refinement (Cruickshank, 1949). Final atomic param-
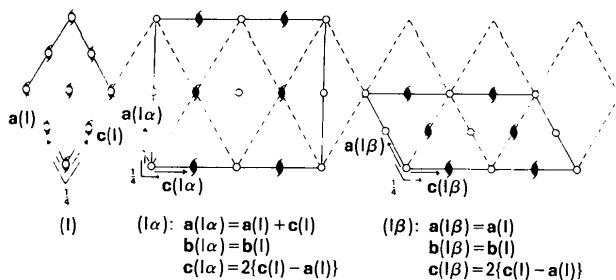
Table 2. *Final positional parameters* ($\times 10^5$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$) *for the non-H atoms for DMM(TCNQ)$_2$* (Iα) *at 95 K*

$U_{eq} = \sum_i U_{ii}/3$ after diagonalization of the U tensor.

	x	y	z	U_{eq}
N(1)	14133 (8)	18229 (4)	−1898 (7)	207 (3)
C(2)	19097 (8)	14673 (4)	−2049 (7)	150 (3)
C(3)	24675 (8)	10075 (4)	−2461 (7)	133 (3)
C(4)	33729 (9)	10171 (4)	−7307 (7)	151 (3)
N(5)	41002 (8)	10197 (4)	−11292 (7)	212 (3)
C(6)	20773 (8)	5628 (4)	1000 (7)	123 (3)
C(7)	25685 (8)	864 (4)	−231 (7)	132 (3)
C(8)	21545 (8)	−3501 (4)	2749 (7)	131 (3)
C(9)	12276 (8)	−3442 (4)	7361 (7)	124 (3)
C(10)	7456 (8)	1329 (4)	8756 (7)	132 (3)
C(11)	11504 (8)	5675 (4)	5704 (7)	130 (3)
N(12)	−8515 (7)	−7675 (4)	19042 (7)	197 (3)
C(13)	−1175 (8)	−7804 (4)	15161 (7)	144 (3)
C(14)	7940 (8)	−7903 (4)	10396 (7)	133 (3)
C(15)	12303 (9)	−12742 (4)	8882 (7)	156 (3)
N(16)	15734 (8)	−16667 (4)	7746 (7)	228 (3)
N(17)	37223 (8)	−17629 (4)	27074 (7)	217 (3)
C(18)	32363 (9)	−14027 (4)	26930 (7)	152 (3)
C(19)	26544 (8)	−9516 (4)	27174 (7)	140 (3)
C(20)	17267 (8)	−9902 (4)	31612 (7)	152 (3)
N(21)	9765 (8)	−10368 (4)	35177 (7)	212 (3)
C(22)	30232 (8)	−4949 (4)	23863 (7)	123 (3)
C(23)	25075 (8)	−279 (4)	25207 (7)	133 (3)
C(24)	28991 (8)	4161 (4)	22340 (7)	131 (3)
C(25)	38272 (8)	4294 (4)	17747 (7)	125 (3)
C(26)	43317 (8)	−392 (4)	16226 (7)	140 (3)
C(27)	39456 (8)	−4827 (4)	19198 (7)	137 (3)
N(28)	58567 (8)	9518 (4)	6079 (7)	222 (3)
C(29)	51294 (8)	9199 (4)	10049 (8)	158 (3)
C(30)	42262 (8)	8894 (4)	14869 (7)	144 (3)
C(31)	37407 (9)	13556 (4)	16671 (8)	178 (3)
N(32)	33457 (9)	17324 (4)	18038 (8)	269 (3)
N(33)	65328 (8)	18837 (4)	26138 (7)	232 (3)
C(34)	69640 (9)	15165 (4)	24735 (7)	160 (3)
C(35)	74502 (8)	10468 (4)	23199 (7)	137 (3)
C(36)	83174 (9)	10482 (4)	17793 (7)	152 (3)
N(37)	90141 (8)	10350 (4)	13432 (7)	209 (3)
C(38)	70416 (8)	5966 (4)	26387 (7)	123 (3)
C(39)	75025 (8)	1202 (4)	24565 (7)	134 (3)
C(40)	70911 (8)	−3185 (4)	27477 (7)	130 (3)
C(41)	61925 (8)	−3166 (4)	32491 (7)	118 (3)
C(42)	57318 (8)	1604 (4)	34332 (7)	130 (3)
C(43)	61426 (8)	5991 (4)	31428 (7)	132 (3)
N(44)	41766 (8)	−7611 (4)	44816 (7)	196 (3)
C(45)	48886 (8)	−7656 (4)	40624 (7)	141 (3)
C(46)	57708 (8)	−7681 (4)	35470 (7)	132 (3)
C(47)	61955 (8)	−12499 (4)	33572 (7)	144 (3)
N(48)	65338 (8)	−16395 (4)	32138 (7)	202 (3)
N(49)	86941 (9)	−18110 (4)	48518 (7)	244 (3)
C(50)	82517 (9)	−14445 (4)	49621 (7)	169 (3)
C(51)	77185 (8)	−9865 (4)	51131 (7)	149 (3)
C(52)	68276 (9)	−10300 (4)	56203 (7)	160 (3)
N(53)	61091 (8)	−10721 (4)	60252 (7)	222 (3)
C(54)	80826 (8)	−5236 (4)	48149 (7)	131 (3)
C(55)	75820 (8)	−604 (4)	50128 (7)	136 (3)
C(56)	79569 (8)	3910 (4)	47457 (7)	133 (3)
C(57)	88577 (8)	4172 (4)	42491 (7)	132 (3)
C(58)	93483 (8)	−472 (4)	40320 (7)	145 (3)
C(59)	89763 (8)	−4989 (4)	43058 (7)	142 (3)
N(60)	108241 (8)	9674 (4)	30453 (7)	220 (3)
C(61)	101193 (8)	9282 (4)	34692 (8)	157 (3)
C(62)	92436 (8)	8849 (4)	39895 (7)	139 (3)
C(63)	87823 (8)	13483 (4)	42429 (8)	159 (3)
N(64)	84105 (8)	17221 (4)	44425 (7)	217 (3)
N(65)	57556 (8)	25228 (3)	17 (7)	139 (3)
C(66)	48828 (9)	24328 (4)	6093 (8)	177 (3)
C(67)	38801 (10)	25475 (4)	1258 (9)	202 (3)
O(68)	37458 (7)	22515 (3)	−6734 (6)	260 (3)
C(69)	45162 (10)	23621 (5)	−12878 (9)	257 (4)
C(70)	55499 (9)	22423 (4)	−8773 (8)	198 (3)

Table 2 (*cont.*)

	x	y	z	U_{eq}
C(71)	59008 (9)	30755 (4)	−1570 (8)	186 (3)
C(72)	67061 (9)	23218 (5)	4547 (9)	217 (3)
N(73)	7567 (8)	25184 (3)	25402 (7)	139 (3)
C(74)	−1376 (9)	24375 (4)	31256 (8)	177 (3)
C(75)	−11208 (10)	25549 (4)	26150 (9)	205 (3)
O(76)	−12353 (7)	22531 (3)	18191 (6)	252 (3)
C(77)	−4456 (10)	23578 (5)	12212 (8)	242 (4)
C(78)	5759 (9)	22358 (4)	16604 (8)	194 (3)
C(79)	9319 (9)	30689 (4)	23756 (8)	196 (3)
C(80)	16829 (9)	23114 (5)	30224 (8)	215 (3)

eters of the non-H atoms are listed in Table 2.* The calculations were carried out with the *XRAY* system (1976); with scattering factors for the H atoms taken from Stewart, Davidson & Simpson (1965) and for the non-H atoms from Cromer & Mann (1968).

Description of the structure

The projection of the (Iα) structure at 95 K in Fig. 2 shows the TCNQ molecules around $y = 0$, and the DMM groups around the c-glide planes at $y = \frac{1}{4}$ and

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* Lists of final positional parameters and isotropic thermal parameters for the H atoms, anisotropic thermal parameters and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42240 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
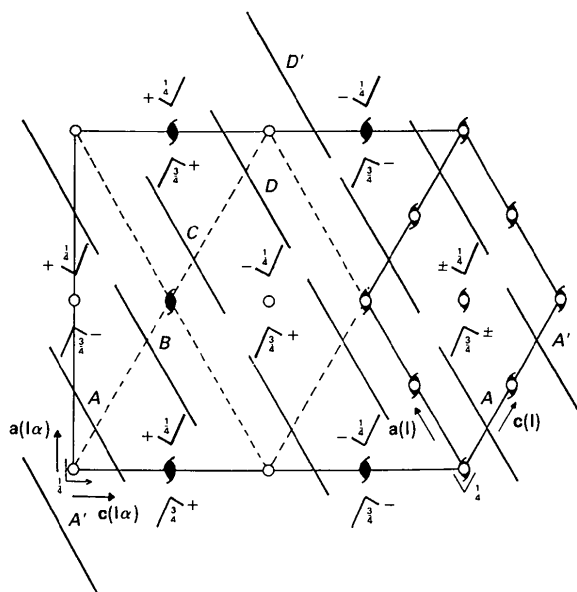

Fig. 2. Schematic drawing of DMM(TCNQ)$_2$ (Iα) at 95 K, seen along [010]. A TCNQ molecule is represented by the line connecting the nitrogens with the largest separation in this projection. A DMM molecule is represented by its height and the projection of the N–CH$_3$ bonds. The cell of (I) is given in bold lines at the right of the figure. For further explanation, see text.

Table 3. *Shift vectors between successive molecules within the TCNQ stack of DMM(TCNQ)$_2$ (Iα) at 95 K, and of DMM(TCNQ)$_2$ (I) at 294 K (Kamminga & van Bodegom, 1981)*

The vectors connect the centres of gravity of the respective molecules and are expressed by the shifts (in Å) along their inertial axes L, M, N (L along the longest molecular axis; M in the molecular plane, perpendicular to L; N at right angles to the plane; see van Bodegom, 1979). For non-parallel successive TCNQs the average shift in each of the L, M, N systems is given.

Intra = Intradimer shift; Inter = Interdimer shift. For numbering see Fig. 2. The standard deviations are estimated to be 0·002 ± or less.

		(Iα)			(I)		
		L	M	N	L	M	N
Inter	A'--A	−1·851	2·623	3·203	−1·638	2·544	3·288
Intra	A-B	0·232	1·072	3·180	0·235	1·059	3·247
Inter	B--C	−1·648	2·506	3·209	−1·638	2·544	3·288
Intra	C-D	0·240	1·067	3·192	0·235	1·059	3·247
Inter	D--D'	−1·330	2·370	3·261	−1·638	2·544	3·288

$y = \frac{3}{4}$. The independent TCNQ molecules are denoted A, B, C and D; the DMM molecules at $z = 0$ and $z = \frac{1}{4}$ are independent. The orientation of the DMMs is characterized by the directions of their N–CH$_3$ bonds. Each DMM has one N–CH$_3$ bond approximately parallel to the *ac* plane, and one N–CH$_3$ bond pointing to either the TCNQ sheet at $y = 0$ or to the sheet at $y = \frac{1}{2}$. A + or − sign at the DMM positions indicates whether the latter N–CH$_3$ bond points 0·056 **b** upwards or downwards. Projections along the [201] (Iα) stacking axis and along [20$\bar{1}$] (Iα) are, apart from the N–CH$_3$ directions, comparable with the full drawings given for the 294 K structure of (I) by Kamminga & van Bodegom (1981). The symmetry elements in Fig. 2 show that the mirror plane at $y = \frac{1}{4}$ in (I) has become a *c*-glide plane in (Iα), with a translation component that corresponds to the translation period **c**(I)−**a**(I) in (I).

The ordering of the DMM molecules

In (I) the DMM molecules are disordered over two symmetrically related positions around the mirror plane at $y = \frac{1}{4}$ or $y = \frac{3}{4}$, corresponding to a random distribution of + and − orientations in Fig. 2. At the phase transition to (Iα) the DMM groups become ordered. At $z = 0$ and $z = \frac{1}{2}$ successive DMM groups in (Iα) are alternately in the + and − orientations. The DMMs at $z = \frac{1}{4}$ all have the + orientation, whereas the − orientation is found at $z = \frac{3}{4}$. The ordering of the DMM molecules does not affect the gross features of the structure. As in (I), the structure of (Iα) still consists of sheets of TCNQ molecules around $y = 0$ and $y = \frac{1}{2}$ with DMMs half-way between the sheets. In both phases, successive sheets along **b** are related by 2$_1$ axes.

The TCNQ stack

In (I) a translation period along **c**(I) contains two TCNQ molecules, A and A', which are related by an inversion centre; the stack is thus dimeric. In (Iα) the stack, along [201](Iα), contains a set of four independent TCNQs, A, B, C and D, related to a second set A', B', C' and D' by the inversion centre

at (0, 0, 0). The stack is thus octameric. At room temperature the angle between the normal of the TCNQ planes and the **c**(I) stacking axis is 30·6°. In (Iα) the corresponding angles with respect to the [201](Iα) axis are 30·78 (3), 30·68 (3), 27·76 (3) and 27·89 (3)° for A, B, C and D, respectively. Further details on the stack geometry are listed in Table 3, which shows that the relative shifts of successive TCNQ molecules are only slightly affected by the ordering of the DMM molecules. The prevailing difference between the stacks of (I) and (Iα), *i.e.* a decrease of the average shift along N by 0·064 Å, can be attributed to the anisotropic thermal expansion of the TCNQ stacks (van Smaalen, de Boer, Haas & Kommandeur, 1985).

Apart from the displacement along N, the intradimer shifts in (Iα) do not differ much from those in (I). This also holds for the interdimer L and M shifts at *B--C*. Around this TCNQ pair, the DMM groups on both sides of the sheet are related by a twofold screw axis, implying that one of the N–CH$_3$ bonds points towards the sheet, whereas the other points away from it. In this respect the situation at *B--C* is comparable with (I), in which the N–CH$_3$ directions towards and away from the sheet have equal probability. For *A'--A*, where the N–CH$_3$ bonds closest to the TCNQ pair both point away from the sheet, the interdimer L and M shifts are larger than in (I), whereas at *D--D'*, where the reverse situation is encountered, the L and M shifts are smaller than in (I).

Molecular geometry and charges ρ

Full tables with the molecular geometries of the present structure have been deposited; in this section we will briefly discuss some general features.

Chemically equivalent bond lengths and angles of the two independent DMM groups do not show significant differences and agree well with the values observed for other substituted morpholinium groups (Bosch & van Bodegom, 1977; Morsink & van Bodegom, 1981; Kamminga & van Bodegom, 1981; van Bodegom & de Boer, 1981).

Table 4. *Average lengths of the equivalent bonds a to e in the TCNQ molecules, and TCNQ charges ρ and ρ_N (see text)*

The estimated standard deviations as deduced from the errors in the atomic positions are 0·002 Å for the bond lengths and 0·03 e for the charges.
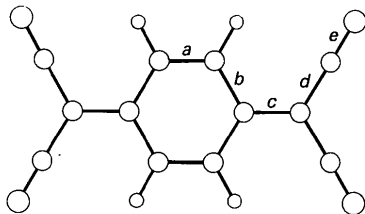
DMM(TCNQ)$_2$ (Iα) at 95 K

	a	b	c	d	e	ρ	ρ_N
TCNQ A	1·359	1·436	1·395	1·427	1·152	0·44	0·42
B	1·362	1·432	1·402	1·424	1·152	0·61	0·58
C	1·362	1·433	1·400	1·426	1·151	0·55	0·52
D	1·362	1·433	1·399	1·428	1·151	0·52	0·49

DMM(TCNQ)$_2$ (I) at 294 K (Kamminga & van Bodegom, 1981)

|	a	b	c	d	e	ρ	ρ_N
TCNQ A	1·350	1·436	1·393	1·425	1·143	0·43	0·50

With respect to the bond lengths, the TCNQ molecules show approximate *mmm* symmetry. Average values of the equivalent bond lengths are given in Table 4. The charges in the table are calculated from the bond lengths according to the method of Flandrois & Chasseau (1977). With the assumption that the morpholinium charge is 1+, so that $\langle\rho(TCNQ)\rangle=\frac{1}{2}$, the normalized values ρ_N are obtained. None of these values deviates significantly from the average value. Least-squares planes were calculated for each of the TCNQ groups using the eight carbon atoms of the quinodimethane skeleton. As found for most other TCNQ complexes the cyano groups are bent out of the quinodimethane planes, with nitrogens at distances of up to 0·45 Å from these planes. Owing to this the molecules adopt a shallow boat form, with cyano groups on both sides of an interdimer overlap (see Table 3) bending towards each other. The same situation was observed at room temperature (Kamminga & van Bodegom, 1981).

Discussion

From Table 3 it is apparent that all overlaps between successive molecules in the TCNQ stacks of (Iα) are comparable with those in (I). The values of the transfer integrals t between neighbouring TCNQ molecules, calculated according to van Smaalen & Kommandeur (1985), are listed in Table 5. In (Iα) the intradimer t values are slightly larger than in (I) because of the decrease in intradimer distance, owing to the difference in temperature. It is noteworthy that for the interdimer shift B--C in (Iα), and thus for the interdimer shift in (I) (see above), a local optimum for the transfer integral is reached, as both smaller

Table 5. *Transfer integrals t (eV) in the octameric TCNQ stack of DMM(TCNQ)$_2$ (Iα) at 95 K and in the dimeric stack of DMM(TCNQ)$_2$ (I) at 294 K*

In (Iα) the stack sequence is

$$-D-[-D'-C'--B'-A'--A-B--C-D-]-D'-.$$
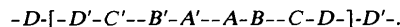
The brackets denote the translation period [201] (Iα); inside the brackets M' is related to M by the inversion centre at (0, 0, 0). Molecules outside the brackets are obtained by translation along [201] (Iα). The t(I) values were calculated from the coordinates reported by Kamminga & van Bodegom (1981).

	t(Iα)	t(I)
A'--A	0·057	0·048
A-$B=A'$-B'	0·172	0·151
B--$C=B'$--C'	0·058	0·048
C-$D=C'$-D'	0·168	0·151
D--D'	0·042	0·048

(at D--D') and larger (at A'--A) shifts cause a decrease of t. The stack region D' to D, in brackets in Table 5, is dimeric in a good approximation, with ratios between successive t values varying from 0·33 to 0·35 [0·32 in (I)]. At D--D' this ratio drops to 0·25. The small difference of 0·015–0·017 eV between $t(D$--$D')$ and the other interdimer t values in (Iα) is comparable with the difference of 0·015 eV between the interdimer t values in the tetrameric TCNQ stacks of the low-temperature phase ($T <$ 17·4 K) of N-ethyl-N-methylmorpholinium–TCNQ [MEM(TCNQ)$_2$] (Visser, Oostra, Vettier & Voiron, 1983). In the latter compound, the slight alternation in the interdimer transfer integral strongly affects the magnetic susceptibility $\chi(T)$ (Huizinga *et al.*, 1979). In analogy to MEM(TCNQ)$_2$, Schwerdtfeger *et al.* (1981) have interpreted $\chi(T)$ of monoclinic DMM(TCNQ)$_2$ by describing the TCNQ stacks at low temperatures as a one-dimensional Heisenberg chain, with one spin localized on each dimer and an alternating antiferromagnetic exchange interaction between the spins. The exchange energy $J = 132$ K,[*] deduced from the $\chi(T)$ curve with use of the above theory, is large in comparison to the J values in other compounds, for instance $J = 53$ K for $t = 0·04$ eV in MEM(TCNQ)$_2$ above $T = 17·4$ K and $J = 30$ K for $t = 0·14$ eV in METM(TCNQ)$_2$ (Oostra & Visser, 1985). There are two tentative explanations for the large J value in monoclinic DMM(TCNQ)$_2$: (1) the uniform charge distribution along the stack, and (2) the fact that, in contrast to the theory applied, the present chain contains a sequence of one weak and three stronger interdimer exchange interactions. Definite conclusions require further theoretical studies. The suggestion that $\chi(T)$ was measured for modification (Iβ) rather than for (Iα) is highly unlikely. The inability to retrieve (Iβ) (see

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[*] This value is half the value mentioned in the original paper (Schwerdtfeger *et al.*, 1981), and was obtained by a redefinition of the magnetic energy, making the exchange interaction of the various compounds in the present paper compatible.

Experimental) and the fact that repeated susceptibility measurements have always given the same result (Oostra, 1984) make it reasonable to assume that the measured $\chi(T)$ curve belongs to the most accessible modification ($I\alpha$).

It is noteworthy that the phase transition of (I) to ($I\alpha$) leads to octameric rather than to tetrameric stacks, as is expected for isolated stacks in which the exchange interaction between the conduction electrons is modified (Huizinga, Kommandeur, Jonkman & Haas, 1982). In the above discussion of the ($I\alpha$) structure the changes in the stack have been attributed to the ordering of the DMM groups, indicating that the phase transition is most probably driven by this ordering. However, it is not clear to what extent the modification of the exchange interactions at T_c also contributes to the stability of the low-temperature structure.

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Compilation of Temperature Factors for Elements and Binary Compounds

The Commission on Neutron Diffraction has initiated a new project for compiling *accurate* temperature factors. The compilation will be restricted to elements and binary compounds. Later, it may be extended to other compounds, replacing the compilation published in Volume III of *International Tables for X-ray Crystallography.*

Interested crystallographers are requested to contact any one of the following:

Dr N. M. Butt, Nuclear Physics Division, PINSTECH, Post Office Nilore, Rawalpindi, Pakistan.

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A copy of a preliminary compilation can be obtained from Dr N. M. Butt.

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Commission on Journals Reporting an Absolute-Configuration Determination

A structural paper reporting an absolute-configuration determination should, if practicable, also report a chiral property of the source material which can be linked uniquely to the structural handedness. If such a linkage is not made, the result should be reported only as a determination of structural handedness or chirality. Should the source material be a product of reactions with condition-dependent stereospecificity, the experimental conditions of the preparation should be given or referenced and a linkage made between the claimed stereospecificity and the structure. In the event that a linkage cannot be made, a disclaimer is necessary stating that the structural handedness may not be representative of the bulk material.