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Changes in the Structure of the 1:2 Complex of *N*-Ethyl-*N*-methylmorpholinium and 7,7,8,8-Tetracyano-*p*-quinodimethane, MEM(TCNQ)$_2$, above Room Temperature. I. Determination of the Structures at 294 and 323 K

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Abstract

Crystals of MEM(TCNQ)$_2$ are triclinic, space group $P1$, with a = 7·773 (8), b = 15·292 (15), c = 6·960 (7) Å, α = 112·34 (6), β = 74·59 (6), γ = 111·85 (6)°, U = 702 Å^3 at 294 K, and a = 7·775 (8), b = 15·290 (15), c = 6·979 (7) Å, α = 112·01 (6), β = 75·00 (6), γ = 111·77 (6)°, U = 707 Å^3 at 323 *K*, Z = 1. Intensities were collected with Zr-filtered Mo radiation on an automatic Nonius CAD-3 diffractometer. Anisotropic least-squares refinements decreased $R_w(F)$ to 0·077 for 2471 reflections at 294 K, and to 0·089 for 1877 reflections at 323 K. The reported structures are compared with the structure at 113 K [Bosch & van Bodegom (1977). *Acta Cryst.* B**33**, 3013–3021]. The individual TCNQ group, as well as the types of overlap between successive TCNQ molecules in the dimerized TCNQ stack, hardly changes between 113 and 323 K; both separations between the TCNQ units increase by 0·07 Å. The major change is the increasing disorder of the MEM group with increasing temperature. With the assumption of two preferred orientations the 100% occupancy of the orientation observed at 113 K decreases to 84% at 294 K and 63% at 323 K. This increase in disorder is used to explain the results of electrical-conductivity measurements.

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Introduction

In the study of a series of 1:2 complexes of *N*-substituted morpholinium and TCNQ most attention has been paid to the complex MEM(TCNQ)$_2$ (MEM = *N*-ethyl-*N*-methylmorpholinium). The compound undergoes two phase transitions, of second order at 19 K, and of first order at 340 K. Various physical properties have been measured for the three phases (Huizinga, Kommandeur, Sawatzky, Kopinga & De Jonge, 1978) and have, together with the phase transitions, been interpreted by Sawatzky, Huizinga & Kommandeur (1978). The transition at 19 K has a strong impact on the magnetic properties, whereas the high-temperature phase transition has a drastic effect on the electronic behaviour. As an example, the conductivity measured along the single-crystal needle axis is shown in Fig. 1 for temperatures ranging from 250 to 375 K (Sawatzky, Huizinga & Kommandeur, 1978). A jump of three orders of magnitude occurs at the transition temperature, 342 K on heating and 338 K on cooling. Above the phase transition the conductivity is weakly temperature dependent and lies between 1·5 and 3·0 Ω^{-1} mm^{-1}. In the ranges 250 to 290 K and 320 to 340 K the conductivity $\sigma(T)$ can be described by the function $\sigma(T) = \sigma_o \exp(-E_{\rm ACT}/kT)$, with an activation energy $E_{\rm ACT}$ = 0·35–0·39 eV. Between these ranges an anomalous behaviour is observed which might be related to the onset of motion of the MEM group as observed in NMR studies (Nechtschein, Huizinga, Oostra, van Bodegom, Sawatzky & Kommandeur, 1981). To study possible structural changes between 290 and 320 K X-ray structure determinations were carried out at 294 and at 323 K, in addition to the earlier determination at 113 K (Bosch & van Bodegom, 1977).

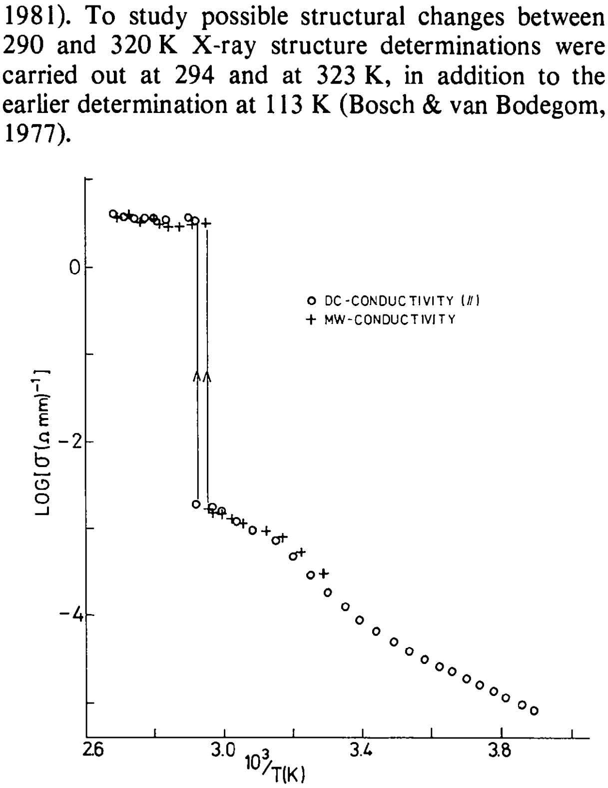

Fig. 1. Single-crystal conductivity of MEM(TCNQ)$_2$ as a function of temperature as measured along the needle (c) axis. DC: four-probe method. MW: microwave method (Morrow, Hardy, Carolan, Berlinsky, Janossy, Holczer, Mihaly, Grüner, Huizinga, Verweij & Sawatzky, 1981).

Experimental

A crystal with regular dimensions 0·4–0·5 mm was used for the measurements. The crystal was heated in a stream of hot air by the use of an apparatus similar to that described by van Bolhuis (1971). Variations in the temperature of the air stream, measured with a copper–constantan thermocouple and recorded continuously during the data collection, were <2 K. The temperature at the position of the crystal was calibrated by the use of the melting points of different materials.

Cell constants

Cell constants and volumes at different temperatures are listed in Table 1(a). In general, the θ, φ and χ values of 12 reflections measured on an automatic Nonius CAD-3 diffractometer were used for the least-squares adjustment. At 294 K the cell constants were also determined with 64 reflections on the CAD-3 diffractometer (III). Comparison of the CAD-3 results (II) and (III) at 294 K shows that the reproducibility of these measurements is better than the e.s.d.'s. Earlier preliminary CAD-4F values at 294 K (I) determined prior to the structure determination at 113 K, for which a, c and β deviate from the present CAD-3 values, will not be considered further. The CAD-3 values in the table show that between 294 and 323 K the lengths of a, b and c do not change significantly. α and β, however, gradually change in the direction of the values found above the phase transition (T_c = 340 K), whereas γ remains almost constant in this temperature interval. Additional crystal data are given in Table 1(b).

Table 1. *Crystal data*

(a) Cell constants of MEM(TCNQ)$_2$ at different temperatures. N_o is the number of observations used in the least-squares program.

		294 K						
	113 K	(I)	(II)*	(III)*	303 K*	313 K*	323 K*	348 K†
a (Å)	7·824 (5)	7·797	7·766	7·773	7·773	7·776	7·775	7·663 (5)
b (Å)	15·426 (16)	15·312	15·302	15·292	15·302	15·308	15·290	15·683 (6)
c (Å)	6·896 (5)	6·989	6·959	6·960	6·969	6·972	6·979	6·584 (6)
α(°)	113·59 (8)	112·42	112·32	112·34	112·28	112·12	112·01	105·97 (3)
β(°)	73·27 (7)	74·38	74·61	74·59	74·61	74·84	75·00	80·35 (7)
γ(°)	112·71 (8)	111·82	111·82	111·85	111·85	111·89	111·77	110·84 (8)
U (Å^3)	695 (2)	708	703 (2)	702 (2)	705 (2)	706 (2)	707 (2)	709 (2)
N_o	34	22	36	192	36	36	36	

* E.s.d.'s are 0·1% for the axes and 0·06° for the angles.

† Values given are averages over 12 determinations of the cell constants during a measurement of the intensities. The unbiased e.s.d.'s are given in parentheses.

(b) Additional crystal data

$C_7H_{16}NO.(C_{12}H_4N_4)_2$, M_r = 538·6, $F(000)$ = 281, Z = 1, d_c = 1·27 (294 K), d_m = 1·25 Mg m^{-3} (294 K). A positive piezoelectric effect at 294 K indicates space group $P1$ at this temperature.

Structure factors

The intensities at 294 and 323 K were collected on an automatic Nonius CAD-3 diffractometer with Zr-filtered Mo radiation by the θ–2θ scan method, and the same crystal. Reflections for one half of reciprocal space of the triclinic crystal were measured up to $\theta = 30°$. Corrections were applied for Lorentz and polarization effects, and for intensity changes of the primary beam from three reference reflections measured at regular intervals.

Corrections for absorption were not made [μ(Mo $K\bar{\alpha}$) = 0·09 mm^{-1}]. Reflections with a net negative intensity were given zero weight. For the remaining reflections the weight w_c was calculated from $w_c = [\sigma_c(F_o)]^{-2}$, $\sigma_c(F_o)$ being the e.s.d. in $|F_o|$ due to counting statistics and errors in the filter factors.

At 294 K, 4118 reflections were measured of which 3293 had $I > 0$. These numbers are 4141 and 2174, respectively, for the measurement at 323 K.

Refinement of the structures

At 113 K the space group is $P1$ with one MEM(TCNQ)$_2$ unit per cell and a pseudo inversion centre between the two TCNQ groups (Bosch & van Bodegom, 1977). During the blocked-matrix least-squares refinement[*] based on the data obtained at 294 and 323 K, atoms related by the pseudo inversion centre were placed in one block to account for correlation effects.

As the refinements revealed disorder for the MEM group different types of refinements were carried out to characterize this disorder. After a description of the details common to all refinements, their differences and results will be discussed.

In all cases the positions of the H atoms were calculated on the basis of geometrical considerations and constrained at 1·08 Å relative to their respective C atoms during the final cycles of refinement. For the non-hydrogen atoms scattering curves were taken from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). The residuals are defined as $R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$, and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ with $w = [\sigma_c^2(F_o) + 0{\cdot}0012|F_o|^2]^{-1}$ for reflections with $|F_o| > 2\sigma_c(F_o)$ and $w = 0$ for the remaining reflections. The goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, in which N_o is the number of reflections included in the refinement and N_v is the number of variables. During the last cycle all parameter shifts were $<0{\cdot}6\sigma$.

Refinement data are summarized in Table 2. The details are as follows.

Table 2. *Comparison of the final results for the refinements of the structure of MEM(TCNQ)$_2$ at* 294 *and* 323 K

Details for each refinement and definitions are given in the text.

Refinement $T = 294$ K, $N_o = 2471$	R	R_w	G	$10^{-4}Q$[*]	N_v	X
A	0·091	0·089	1·45	0·44	379	
B	0·140	0·158	2·48	1·38	231	
C	0·102	0·099	1·56	0·54	245	0·862 (2)
D	0·081	0·076	1·24	0·32	393	0·837 (2)
E	0·081	0·077	1·26	0·33	380	0·841 (5)
$T = 323$ K, $N_o = 1877$						
A	0·108	0·112	2·06	0·64	379	
B	0·112	0·120	2·09	0·72	231	
C[†]	0·115	0·126	2·21	0·80	245	0·701 (2)
D	0·086	0·088	1·62	0·39	389	0·692 (2)
E	0·088	0·089	1·64	0·40	376	0·627 (11)

[*] $Q = \sum w(|F_o| - |F_c|)^2$.

[†] During the final cycles the temperature factor of N(33) of the MEM group tended to go negative. It was set positive by the least-squares program.

(*A*) Refinement in $P1$ starting from the final coordinates of the 113 K structure. For the TCNQ H atoms isotropic thermal parameters were refined. For the MEM H atoms isotropic thermal parameters were estimated from the anisotropic thermal parameters of the heavy atoms by means of a **TLS** rigid-body analysis of the MEM group with the program *TMA* (Shmueli, 1972), and constrained during the last refinement cycles. (Within their large e.s.d.'s, refined MEM H isotropic thermal parameters are equal to the constrained values.) The final difference map showed peaks at positions related to those of the heavy MEM atoms by the pseudo inversion centre. The highest peak of 0·49 e Å^{-3} at 294 K (0·43 e Å^{-3} at 323 K) was related to the O atom. The e.s.d. $\sigma_d = (2\sum \Delta^2)^{1/2}/V$ (Cruickshank, 1949) is 0·05 e Å^{-3} at 294 K and 0·09 e Å^{-3} at 323 K.

(*B*) Refinement in $P\bar{1}$ with MEM randomly disordered over the two symmetrically related positions. H thermal parameters were treated as under (*A*).

(*C*) Positions and thermal parameters in $P\bar{1}$ as for (*B*), but unequal populations x and $1 - x$ for the two MEM groups. MEM H isotropic thermal parameters were varied, except those of the ethyl CH$_3$ group which were constrained at the values estimated under (*A*).

(*D*) No symmetry assumed between TCNQ heavy atoms, but inversion symmetry adopted for the positions and thermal parameters of the two MEM groups with populations x and $1 - x$. MEM H atoms treated as under (*A*). At 323 K also the isotropic H thermal parameters of the TCNQ groups were related by the pseudo inversion centre, as otherwise negative values occurred in some cases.

(*E*) Refinement in $P1$ with fixed positions and thermal parameters of the MEM group with the smallest population $1 - x$. Refinement of TCNQ and MEM (population x) positions and thermal parameters as under (*A*).

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[*] Unless mentioned otherwise calculations were performed with the XRAY system (1976).

Table 3. *Final parameters for MEM(TCNQ)$_2$, at* 294 *and* 323 K

Hydrogen atoms were constrained to the respective C atoms. For numbering of atoms, see Figs. 2 and 3. $U_{eq} = \sum_i U_{ii}/3$ after diagonalization of the **U** tensor. TCNQ coordinates are multiplied by 10^4; U_{eq} (Å^2) values are multiplied by 10^3.

	x		y		z		U_{eq}	
	294 K	323 K	294 K	323 K	294 K	323 K	294 K	323 K
N(1)	3079 (9)	3069 (16)	4298 (5)	4286 (9)	3673 (11)	3643 (23)	80 (3)	121 (6)
C(2)	3299 (9)	3249 (15)	3552 (6)	3561 (8)	3487 (11)	3500 (18)	64 (3)	72 (4)
C(3)	3522 (9)	3494 (13)	2636 (4)	2653 (8)	3203 (10)	3291 (18)	53 (2)	79 (4)
C(4)	5367 (10)	5344 (21)	2687 (5)	2702 (8)	3208 (13)	3402 (22)	72 (3)	113 (5)
N(5)	6843 (8)	6863 (15)	2709 (5)	2691 (8)	3408 (12)	3389 (23)	90 (3)	109 (5)
C(6)	2050 (7)	2077 (11)	1762 (3)	1773 (7)	2918 (7)	2924 (14)	33 (2)	48 (3)
C(7)	2337 (9)	2312 (17)	855 (5)	785 (8)	2672 (10)	2640 (20)	54 (2)	78 (4)
C(8)	871 (8)	848 (12)	25 (4)	−14 (6)	2477 (10)	2409 (14)	48 (2)	46 (3)
C(9)	−936 (7)	−966 (12)	−9 (4)	−31 (6)	2426 (9)	2419 (14)	36 (2)	45 (3)
C(10)	−1204 (7)	−1222 (8)	897 (4)	879 (5)	2668 (9)	2630 (11)	45 (2)	54 (3)
C(11)	234 (8)	176 (12)	1753 (5)	1720 (8)	2838 (11)	2782 (16)	52 (2)	60 (4)
N(12)	−5752 (10)	−5789 (17)	−868 (5)	−921 (10)	2303 (13)	2294 (22)	88 (3)	125 (6)
C(13)	−4335 (8)	−4283 (16)	−887 (4)	−879 (8)	2220 (12)	2222 (21)	53 (2)	78 (5)
C(14)	−2455 (9)	−2439 (13)	−875 (5)	−890 (8)	2248 (10)	2114 (16)	50 (2)	68 (4)
C(15)	−2230 (9)	−2137 (14)	−1809 (5)	−1803 (7)	1977 (10)	1996 (18)	53 (2)	70 (4)
N(16)	−2033 (8)	−2073 (13)	−2522 (4)	−2519 (7)	1849 (10)	1884 (17)	73 (3)	81 (4)
N(17)	−2994 (10)	−3006 (16)	−4293 (5)	−4296 (7)	−3673 (11)	−3670 (16)	87 (3)	93 (4)
C(18)	−3240 (9)	−3239 (14)	−3572 (4)	−3546 (8)	−3428 (11)	−3425 (18)	58 (2)	72 (4)
C(19)	−3532 (7)	−3512 (13)	−2659 (4)	−2653 (6)	−3225 (10)	−3213 (13)	49 (2)	53 (3)
C(20)	−5321 (8)	−5291 (12)	−2701 (4)	−2684 (6)	−3474 (9)	−3353 (17)	52 (2)	52 (3)
N(21)	−6751 (9)	−6686 (18)	−2739 (5)	−2742 (10)	−3572 (11)	−3635 (21)	90 (3)	108 (5)
C(22)	−2062 (9)	−2028 (15)	−1777 (5)	−1770 (8)	−2899 (11)	−2936 (15)	61 (3)	58 (3)
C(23)	−2277 (7)	−2252 (10)	−855 (4)	−908 (6)	−2709 (9)	−2741 (12)	42 (2)	38 (3)
C(24)	−845 (8)	−869 (16)	19 (4)	−12 (10)	−2423 (8)	−2509 (19)	45 (2)	77 (4)
C(25)	1031 (9)	997 (13)	5 (5)	7 (7)	−2444 (10)	−2442 (17)	55 (3)	59 (3)
C(26)	1268 (9)	1272 (12)	−924 (4)	−942 (5)	−2631 (10)	−2672 (11)	52 (2)	65 (3)
C(27)	−189 (8)	−238 (13)	−1758 (4)	−1771 (5)	−2878 (10)	−2924 (14)	46 (2)	53 (3)
N(28)	5835 (8)	5792 (12)	897 (5)	867 (6)	−2245 (14)	−2187 (21)	91 (3)	98 (5)
C(29)	4285 (11)	4329 (15)	891 (5)	873 (8)	−2207 (11)	−2220 (18)	63 (3)	65 (4)
C(30)	2495 (8)	2537 (10)	876 (4)	888 (5)	−2148 (9)	−2229 (15)	45 (2)	44 (3)
C(31)	2287 (8)	2345 (11)	1786 (5)	1792 (7)	−1960 (10)	−1953 (14)	56 (2)	55 (3)
N(32)	2133 (9)	2122 (14)	2537 (4)	2566 (7)	−1753 (10)	−1637 (17)	73 (2)	81 (4)
H(C7)	3690	3665	812	742	2666	2634		
H(C8)	1093	1070	−651	−690	2354	2286		
H(C10)	−2594	−2612	905	888	2718	2679		
H(C11)	−7	−66	2425	2393	2970	2914		
H(C23)	−3662	−3637	−879	−930	−2773	−2805		
H(C24)	−1104	−1128	700	669	−2197	−2283		
H(C26)	2634	2638	−942	−959	−2607	−2648		
H(C27)	40	−9	−2430	−2443	−2988	−3035		

MEMα coordinates and U_{eq} (Å^2) multiplied by 10^3. Parameters for MEM β atoms were not refined and have been deposited.

	x		y		z		U_{eq}	
	294 K	323 K	294 K	323 K	294 K	323 K	294 K	323 K
N(33)α	34 (1)	−5 (3)	494 (1)	503 (1)	4 (1)	10 (3)	67 (2)	103 (4)
C(34)α	238 (1)	229 (2)	494 (0)	495 (1)	−52 (1)	−52 (2)	71 (3)	85 (6)
C(35)α	364 (1)	321 (3)	584 (1)	588 (2)	89 (1)	106 (3)	78 (3)	132 (12)
C(36)α	173 (1)	168 (2)	681 (1)	680 (1)	131 (1)	131 (3)	91 (4)	110 (7)
C(37)α	37 (1)	38 (2)	590 (1)	592 (1)	−10 (1)	−23 (3)	78 (3)	113 (9)
C(38)α	−46 (1)	−54 (3)	480 (1)	489 (2)	212 (2)	213 (3)	135 (5)	168 (9)
C(39)α	−68 (1)	−75 (2)	407 (1)	409 (1)	−162 (1)	−164 (3)	93 (3)	107 (7)
C(40)α	−278 (2)	−324 (4)	392 (1)	406 (2)	−124 (2)	−67 (6)	116 (5)	221 (18)
Oα	354 (1)	348 (1)	670 (1)	674 (1)	61 (1)	69 (2)	81 (2)	103 (5)

Table 2 shows that at 294 K the centrosymmetric structure model having for MEM $x = 1 - x = 0{\cdot}50$ is clearly worse than the completely asymmetric structure with $x = 1$. At 323 K the $|F_c|$ values for both models show about the same agreement with $|F_o|$. At both temperatures the G values become significantly closer to unity if, in space group $P1$, MEM is assumed to be disordered over two pseudo centrosymmetrically related positions, but with unequal populations. Model (*E*) is preferred to model (*D*) as the lack of centrosymmetry of the structure is emphasized best in (*E*). Final positional parameters are given in Table 3.*

Discussion

Three-dimensional packing

In comparison with the 113 K structure the overall packing has changed so little that the pictures given for the packing at 113 K are still valid at higher temperatures. The structure contains dimerized stacks $B\cdots A\cdots B'\cdots A'$ ($B'\cdots A'$ translationally equivalent with $B\cdots A$) in which the intradimer overlap $A\cdots B$ is much larger than the interdimer overlap $A\cdots B'$. Table 4 shows that between 113 and 294 K the distances between the TCNQ groups increase by 0·05 Å as has also been observed for $Rb_2(TCNQ)_3$ (van der Wal & van Bodegom, 1979) and Rb(TCNQ)-I (van Bodegom, 1979). The absolute values of the shifts of the TCNQ planes of *A* and *B* relative to each other decrease slightly with increasing temperature, resulting in a small increase of the interdimer overlap $A\cdots B'$. The intradimer overlap $A\cdots B$ decreases slightly.

Table 4. *Shifts* (Å) *of TCNQ B and B′ relative to TCNQ A as seen along the normal to the p-quinodimethane plane, distances* (Å) *between these planes and angles of their normals with the c axis at* 113, 294 *and* 323 K

$S(\perp)$: shift perpendicular to the longest molecular axes; $S(\parallel)$: shift along these axes. Values without parentheses are defined relative to the normal of TCNQ *A*, and those in parentheses relative to the normal of TCNQ *B*. The averages of two corresponding values are also listed. E.s.d.'s are ≤2 in the last digit shown.

T (K)	$S(\perp)$	$\langle S(\perp)\rangle$	$S(\parallel)$	$\langle S(\parallel)\rangle$	d*	$\langle d\rangle$
TCNQ *A* and *B*						
113	0·15 (0·10)	0·13	−1·95 (−1·99)	−1·97	3·16 (3·14)	3·15
294	0·15 (0·16)	0·16	−1·95 (−1·99)	−1·97	3·21 (3·19)	3·20
323	0·16 (0·17)	0·16	−2·01 (−2·03)	−2·02	3·20 (3·23)	3·22
TCNQ *A* and *B′*						
113	2·54 (2·60)	2·57	−2·24 (−2·19)	−2·22	3·30 (3·28)	3·29
294	2·51 (2·52)	2·51	−2·15 (−2·09)	−2·12	3·33 (3·36)	3·35
323	2·47 (2·49)	2·48	−2·08 (−2·11)	−2·10	3·38 (3·35)	3·36

Angles (°) between the normal **N** to the quinodimethane planes and the *c* axis and mutual angles (°) between normals

	113 K	294 K	323 K
$L(\mathbf{N}_A, \mathbf{c})$	20·5	19·9	19·4
$L(\mathbf{N}_B, \mathbf{c})$	21·3	19·8	19·5
$L(\mathbf{N}_A, \mathbf{N}_B)$	1·2	0·6	0·9

* For definition of *d*, see van Bodegom & de Boer (1981).

The MEM group

The major change in the structure is the increasing disorder of the MEM group with temperature. In the refinement this disorder has been described by assuming the presence of two preferred orientations with occupancies x and $1-x$, but the presence of subsidiary positions with low occupancy cannot be excluded. The occupancy x decreases from 1·0 at 113 K to 0·84 at 294 K and 0·63 at 323 K. Between 294 and 323 K the increase in disorder is observed in the same crystal, indicating that the MEM group can overcome the potential barrier between the two positions. The dynamical character of the increasing disorder between 294 and 323 K is in agreement with NMR measurements, which show an increase of the motional narrowing of the MEM proton peaks with temperature in this range (Nechtschein, Huizinga, Oostra, van Bodegom, Sawatzky & Kommandeur, 1981). The MEM geometry is given in Fig. 2. The molecule has retained the chair form. Owing to the disorder the molecular geometry is so inaccurate that it will not be discussed further.

The TCNQ groups

In the 113 K structure the molecular geometry of the TCNQ groups indicates that molecule *A* carries more charge than molecule *B*. This will be due to a difference in location relative to the MEM group. Indeed the oxygen side of MEM has shorter contacts to TCNQ *B* and the $C_2H_5N^+$ part to TCNQ *A*. The increase of the dynamical disorder of the MEM group from 294 to 323 K makes the (average) location of MEM relative to the two TCNQ groups more equivalent. It is therefore expected that at higher temperatures the geometry of the two TCNQ groups will become more equal. The geometrical data are given in Fig. 3. Because of the

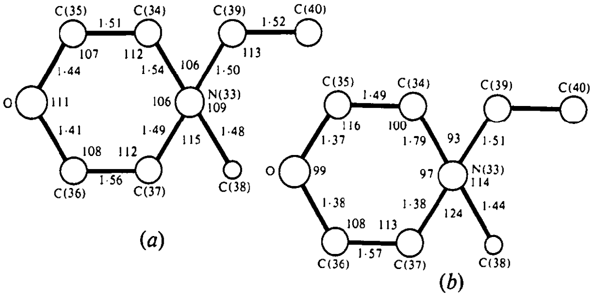

Fig. 2. Molecular geometry of the MEM molecule in $MEM(TCNQ)_2$ at 294 and 323 K. Values for bond lengths are in Å, and for angles in degrees. The least-squares e.s.d.'s have been omitted, as they strongly underestimate the errors in the molecular geometry caused by the disorder of the MEM. (*a*) 294 K, (*b*) 323 K.

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* Lists of structure factors, coordinates of MEM β heavy atoms and MEM hydrogen atoms, and thermal parameters obtained at 294 and 323 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35696 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

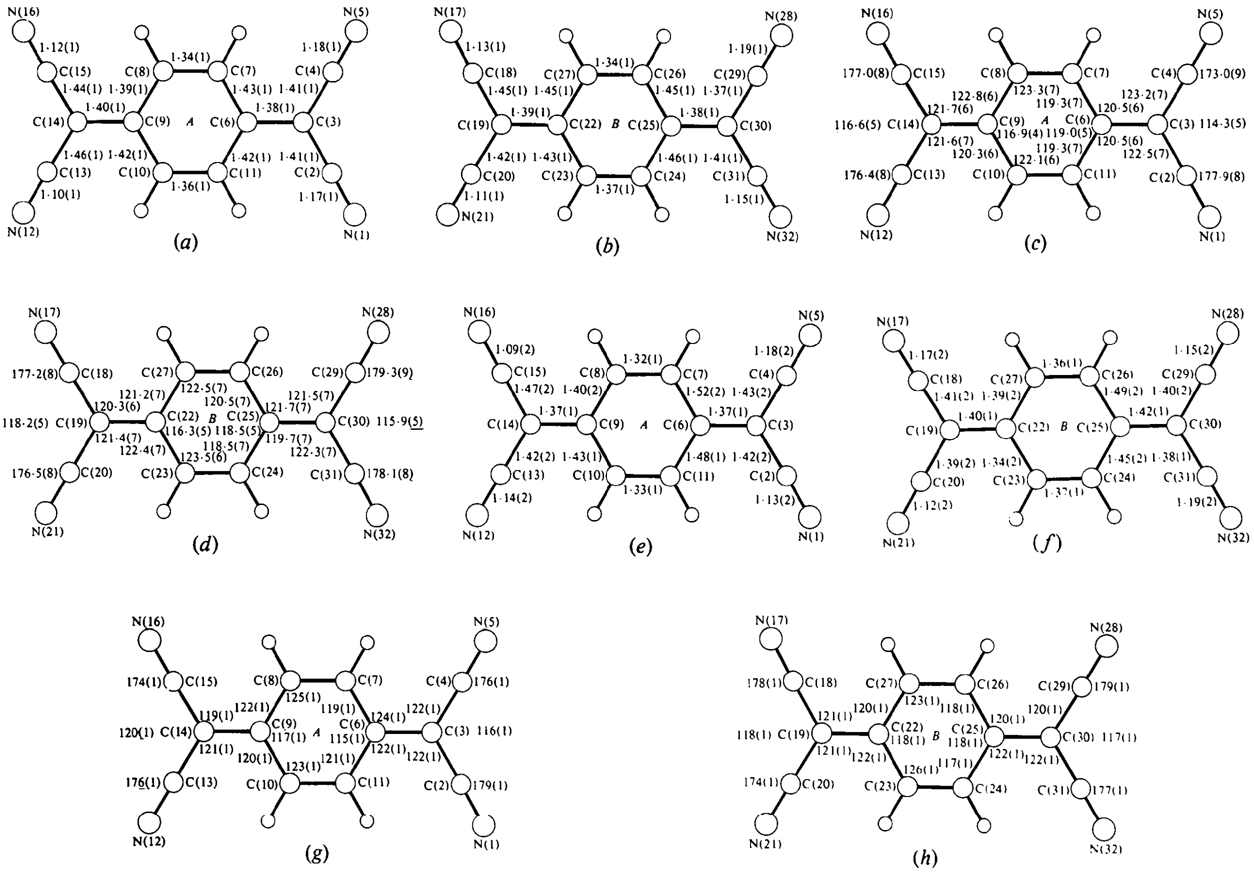

Fig. 3. Molecular geometry of the TCNQ units in MEM(TCNQ)$_2$ at 294 and 323 K. Values for bond lengths (Å) and angles (°) are not corrected for libration effects. Bond lengths (294 K): (*a*) molecule *A*, (*b*) molecule *B*. Bond angles (294 K): (*c*) molecule *A*, (*d*) molecule *B*. Bond lengths (323 K): (*e*) molecule *A*, (*f*) molecule *B*. Bond angles (323 K): (*g*) molecule *A*, (*h*) molecule *B*.

large thermal motion, the MEM disorder and the correlation between the TCNQ groups the data are not sufficiently accurate, however, to check whether or not the small differences noticed at 113 K have vanished.

Electrical conductivity

The fact that the activation energies below 290 and above 320 K are essentially the same suggests that the increase in conductivity between 290 and 320 K is not due to a decrease in activation energy, but to an increase in the mobility. In simplified terms the following tentative explanation can be given for this phenomenon. At 113 K the charge of 1 e is not distributed evenly over the dimers $A\cdots B$, but is slightly concentrated on *A*. This reduces the mobility. In the limiting case of an infinitely high electric potential at *A*, in comparison with *B*, the electron density would be completely concentrated at *A* and the mobility would be zero (or in terms of band theory with dimeric entities $A'-B'\cdots A-B$ *etc.*: as *B* has no charge density to overlap with *A* the bandwidth decreases to zero). The increase in disorder of the MEM group between 290 and 323 K decreases the potential difference between *A* and *B*. The tendency of the electron to be concentrated on *A* is therefore reduced, which may result in an increase of the mobility. A more quantitative elaboration of this idea will be published elsewhere (Nechtschein, Huizinga, Oostra, van Bodegom, Sawatzky & Kommandeur, 1981). This idea does not explain, however, the large increase of σ at 340 K. The investigation of this phenomenon by determination of the structure above the phase transition is reported in the following paper.

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Changes in the Structure of the 1:2 Complex of *N*-Ethyl-*N*-methylmorpholinium and 7,7,8,8-Tetracyano-*p*-quinodimethane, MEM(TCNQ)$_2$, above Room Temperature. II. Determination of the Structure (above the Phase Transition) at 348 K

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Abstract

Crystals of MEM(TCNQ)$_2$ above the high-temperature phase transition at $T_c = 340$ K are triclinic, with (at 348 K) $a = 7{\cdot}666\,(3)$, $b = 15{\cdot}684\,(3)$, $c = 6{\cdot}585\,(5)$ Å, $\alpha = 105{\cdot}97\,(1)$, $\beta = 80{\cdot}33\,(3)$, $\gamma = 110{\cdot}86\,(3)^\circ$, $U = 709$ Å^3. Intensities were collected at 348 K with Zr-filtered Mo radiation on a Nonius CAD-4F diffractometer. The structure was solved in space group $P\bar{1}$ under the assumption of random disorder for the MEM group over two centrosymmetrically related orientations. Anisotropic least-squares refinement with $w = 1$ gave $R_F = 0{\cdot}082$ for 1233 reflections. The disorder of the MEM group is enhanced at the phase transition. The strongly dimerized TCNQ stacks below T_c become nearly regular above T_c with TCNQ distances of 3·29 (1) Å and overlap approaching the ring–external-bond type. The strong conductivity above T_c is tentatively explained by the regularity of the stack and the uniform charge distribution along the stack due to the MEM disorder, but work on further TCNQ compounds is required to make this explanation definite. The bending of the crystal observed macroscopically around T_c has been related to the microscopic structural changes during the phase transition.

Introduction

In the previous paper the increase in dynamical disorder of the MEM group observed by X-ray diffraction and NMR spectroscopy (van Bodegom, 1981; Nechtschein, Huizinga, Oostra, van Bodegom, Sawatzky & Kommandeur, 1981) has been correlated with the anomalous increase of the electrical conduc-

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