

A uniform and one-dimensional stacking of 2,5-dichlorotetracyanoquinodimethane molecules in the tetramethylarsonium salt

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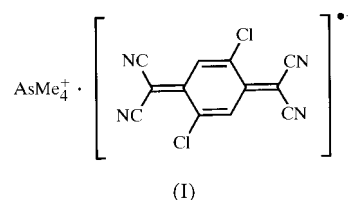
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In the tetramethylarsonium salt of 2,5-dichloro-7,7,8,8-tetracyanoquinodimethane [systematic name: tetramethylarsonium 2,2'-(2,5-dichlorocyclohexa-2,5-diene-1,4-diylidene)bis-(propanedinitrile)], $C_4H_{12}As^+ \cdot C_{12}H_2Cl_2N_4^-$ or $[As(CH_3)_4] \cdot (C_{12}H_2Cl_2N_4)$, the cation lies disordered about a twofold axis and the radical ion lies about an inversion center forming a uniform [interplanar distance 3.35 (2) Å] and one-dimensional stacking without any slip. The electrical conductivity of the single crystal at room temperature was less than 10^{-9} S cm⁻¹, and the temperature dependence of paramagnetic susceptibility obeyed a one-dimensional antiferromagnetic Heisenberg model with a spin-exchange integral of 83 K in the temperature range 1.8–320.0 K.

Comment

Tetracyanoquinodimethane (TCNQ), one of the familiar electron-acceptor molecules, can readily capture one electron to produce the corresponding radical anion (TCNQ⁻), which has been isolated as alkali metal cation, ammonium, phosphonium and arsonium salts (Hoekstra *et al.*, 1972; Konno & Saito, 1974; Konno *et al.*, 1977). X-ray crystal structure determinations at room temperature and/or low temperatures were carried out for these salts, and dimerization of TCNQ⁻ molecules was observed in all cases, except for the *N*-methylphenazinium (NMP⁺) salt with a triclinic phase (Fritchie, 1966; Coleman *et al.*, 1972; Kobayashi, 1975; Morosin, 1975), in which TCNQ⁻ molecules formed a uniform and one-dimensional stacking at room temperature. The stacking structure of TCNQ⁻ molecules is strongly related to the electrical conducting properties of the salts. Thus, all the salts with a dimerized structure exhibited a semiconducting or insulating property, while for the NMP⁺ salt, the electrical conductivity at room temperature was not only very high (170 S cm⁻¹; Melby, 1965), but the temperature

dependence of the electrical conductivity was also like a metal in the temperature range 200–300 K, where a metal-to-insulator transition due to preferential dimerization occurred (Epstein *et al.*, 1972; Coleman *et al.*, 1973). A stable uniform and one-dimensional stacking structure of TCNQ⁻ molecules is necessary in order to achieve a new metallic conducting TCNQ⁻ salt and further to maintain the metallic state down to the liquid helium temperature. Introduction of a sterically bulky substituent to the TCNQ skeleton is the simplest approach to suppress the dimerization. We now report that a uniform and one-dimensional stacking structure can be produced by dichloro-substituted TCNQ⁻ (Cl₂TCNQ⁻) molecules.



Figs. 1, 2 and 3 show an ellipsoid plot of the tetramethylarsonium (AsMe₄⁺) salt of Cl₂TCNQ⁻ (AsMe₄⁺·Cl₂TCNQ⁻), the crystal structure viewed along the *a* and *c* axes, and the stacking of Cl₂TCNQ⁻ molecules in the crystal, respectively. The AsMe₄⁺ ion lies on a twofold axis and the Cl₂TCNQ⁻ molecule lies on a center of inversion. The AsMe₄⁺ ions and Cl₂TCNQ⁻ molecules form alternating layers along the *b* axis. Two of the four methyl groups in the AsMe₄⁺ ion are disordered. Each of the AsMe₄⁺ ions is located between two Cl₂TCNQ⁻ molecular planes. The dihedral angle between the six-membered ring and the C(CN)₂ group is 1.4 (2)°. As a

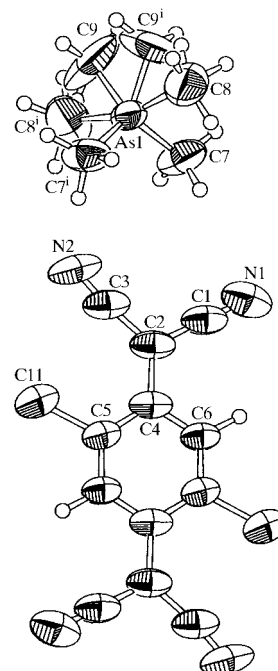


Figure 1

Displacement ellipsoid plot of the title salt with ellipsoids at the 50% probability level. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

result, the Cl_2TCNQ^- molecule is almost planar. The present molecule is more planar than molecules of the TCNQ^- salts with a dimerized structure, such as $\text{Na}^+\cdot\text{TCNQ}^-$ (corresponding dihedral angle: 5° ; Konno & Saito, 1974), and comparable to that of $\text{NMP}^+\cdot\text{TCNQ}^-$ with a triclinic phase. The Cl_2TCNQ^- molecules stack without any slip to form a uniform and one-dimensional array along the c axis, although the long axes of the molecules are alternately inclined by a small angle of 18° . The interplanar distance is $3.35(2) \text{ \AA}$, which is slightly shorter than 'a π -cloud thickness' (3.40 \AA). It is noteworthy that the stacking structure of Cl_2TCNQ^- molecules compares with that of TCNQ^- molecules in the triclinic phase of $\text{NMP}^+\cdot\text{TCNQ}^-$; the stacking of TCNQ^- molecules has a slipped structure, with a distance of 2.09 \AA between the centers of the six-membered rings. It is remarkable that the interplanar distance is fairly short (3.26 \AA) compared with 'a π -cloud thickness'.

The electrical conductivity of the single crystal at room temperature was less than $10^{-9} \text{ S cm}^{-1}$. In addition, the temperature dependence of paramagnetic susceptibility obeyed a one-dimensional antiferromagnetic Heisenberg model with a spin-exchange integral of 83 K in the temperature range $1.8\text{--}320.0 \text{ K}$. These results suggest that both spin and negative charge are localized on each Cl_2TCNQ^- molecule. The electrical conducting and magnetic properties of $\text{AsMe}_4^+\cdot\text{Cl}_2\text{TCNQ}^-$ are remarkably different from those of

$\text{NMP}^+\cdot\text{TCNQ}^-$, *i.e.* metallic conductivity and Pauli paramagnetism between 200 and 300 K . It is conceivable that a special uniform and one-dimensional stacking structure is responsible for the metallic conductivity in the TCNQ^- salts.

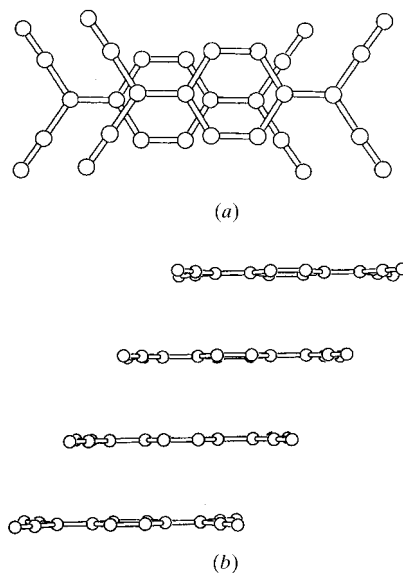


Figure 3 Schematic stacking of the TCNQ^- molecules in $\text{NMP}^+\cdot\text{TCNQ}^-$ shown through (a) a top and (b) a side view (Fritchie, 1966; Coleman *et al.*, 1972; Kobayashi, 1975; Morosin, 1975).

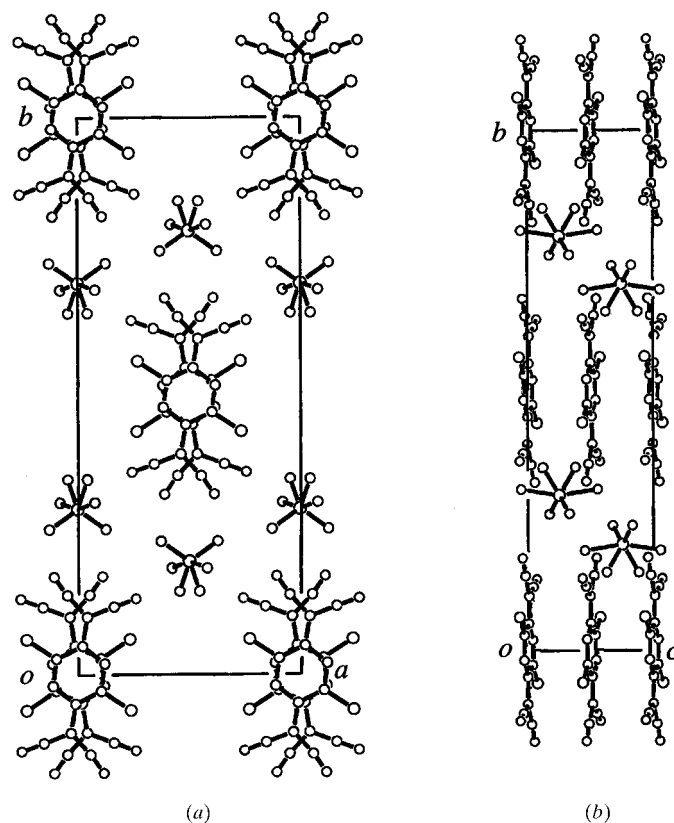


Figure 2 The crystal structure of $\text{AsMe}_4^+\cdot\text{Cl}_2\text{TCNQ}^-$ viewed along (a) the c and (b) the a axis. Two of the four methyl groups in the AsMe_4^+ ion are disordered.

Experimental

After Cl_2TCNQ (Wheland & Martin, 1975) was reacted with LiI in CH_3CN , the Li^+ salt of Cl_2TCNQ^- obtained was converted to the AsMe_4^+ salt by treatment with an excess of $\text{AsMe}_4^+\cdot\text{I}^-$ in H_2O . The crude $\text{AsMe}_4^+\cdot\text{Cl}_2\text{TCNQ}^-$ salt was recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ to afford the single crystal used for analysis (m.p. $> 573 \text{ K}$).

Crystal data

$[\text{As}(\text{CH}_3)_4](\text{C}_{12}\text{H}_2\text{Cl}_2\text{N}_4)$
 $M_r = 408.14$
 Monoclinic, $C2/c$
 $a = 11.046(3) \text{ \AA}$
 $b = 27.336(4) \text{ \AA}$
 $c = 6.707(6) \text{ \AA}$
 $\beta = 97.45(4)^\circ$
 $V = 2007(1) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.350 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 12.9\text{--}14.8^\circ$
 $\mu = 1.962 \text{ mm}^{-1}$
 $T = 296.2 \text{ K}$
 Prismatic, purple
 $0.20 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.668$, $T_{\max} = 0.675$
 2434 measured reflections
 2323 independent reflections
 1157 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.011$
 $\theta_{\max} = 27.54^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 35$
 $l = -8 \rightarrow 8$
 3 standard reflections
 every 200 reflections
 intensity decay: 10.0%

Refinement

Refinement on F
 $R = 0.063$
 $wR = 0.091$
 $S = 1.95$
 1157 reflections
 114 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o) + 0.00096|F_o|^2]$
 $(\Delta/\sigma)_{\max} = 0.0023$
 $\Delta\rho_{\max} = 0.78 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1—C5	1.735 (8)	C2—C4	1.454 (9)
N1—C1	1.16 (1)	C4—C5	1.42 (1)
N2—C3	1.12 (1)	C4—C6	1.39 (1)
C1—C2	1.41 (1)	C5—C6 ⁱ	1.336 (8)
C2—C3	1.45 (1)		
N1—C1—C2	179.4 (10)	C2—C4—C6	119.2 (8)
C1—C2—C3	111.8 (7)	C5—C4—C6	115.5 (6)
C1—C2—C4	119.8 (8)	C11—C5—C4	120.6 (5)
C3—C2—C4	128.4 (8)	C11—C5—C6 ⁱ	116.1 (6)
N2—C3—C2	172 (1)	C4—C5—C6 ⁱ	123.3 (7)
C2—C4—C5	125.3 (7)	C4—C6—C5 ⁱ	121.2 (7)
C11—C5—C4—C2	−1 (1)	C2—C4—C5—C6 ⁱ	179.6 (7)
C11—C5—C4—C6	179.4 (5)	C2—C4—C6—C5 ⁱ	−179.7 (7)
C11—C5—C6 ⁱ —C4 ⁱ	−179.5 (5)	C3—C2—C4—C5	0 (1)
C1—C2—C4—C5	−179.0 (7)	C3—C2—C4—C6	179.1 (7)
C1—C2—C4—C6	0 (1)		

 Symmetry code: (i) $-x, -y, 1 - z$.

H-atom positions were calculated at C—H distances of 0.95 Å and they were included in the final calculations but not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN*

(Molecular Structure Corporation, 1985b); program(s) used to solve structure: *SIR92*; program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1116). Services for accessing these data are described at the back of the journal.

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