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N-Methylphenazinium 2,5-dichloro-7,7′,8,8′-tetracyanoquinodimethanide

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Key indicators

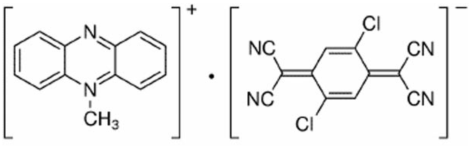
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.122
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{13}H_{11}N_2^+\cdot C_{12}H_2Cl_2N_4^{\cdot -}$, the *N*-methylphenazinium cations have a dimerized structure with an interplanar distance of 3.42 (9) Å without effective overlap between the dimers. On the other hand, the 2,5-dichloro-7,7′,8,8′-tetracyanoquinodimethanide radical anions form a one-dimensional columnar structure along the *a* axis. In the column, there are two different kinds of modes in the overlap of the molecules: one mode has a slipped structure along a longer molecular axis of the molecules, whose six-membered rings are shifted by 2.14 (8) Å, and in the other mode, the $C(CN)_2$ groups are only overlapped with each other. The modes have interplanar distances of 3.11 (4) and 3.19 (2) Å, respectively.

Comment

Much attention has been directed toward 7,7′,8,8′-tetracyanoquinodimethanide radical anion (TCNQ$^{\cdot -}$) salts with alkali metal, ammonium, phosphonium and arsonium ions *etc.* for developing high electrical conducting organic materials (Hoekstra *et al.*, 1972; Konno & Saito, 1974; Konno *et al.*, 1977). For the TCNQ$^{\cdot -}$ salts, the TCNQ$^{\cdot -}$ molecules are usually dimerized and stacked one-dimensionally. As a result of such a structural feature, the room-temperature electrical conductivities are very low (< 10^{-2} S cm^{-1}). Nevertheless, as an exception, an *N*-methylphenazinium salt of TCNQ$^{\cdot -}$ (NMP$^+\cdot$TCNQ$^{\cdot -}$) exhibits very high room-temperature electrical conductivity of 170 S cm^{-1} (Fritchie, 1966; Coleman *et al.*, 1972; Kobayashi, 1975). In the crystals of NMP$^+\cdot$TCNQ$^{\cdot -}$ at room temperature, the TCNQ$^{\cdot -}$ molecules form a uniform and one-dimensional stacking. Although the temperature dependence of electrical conductivity is metallic at 200–300 K, a metal-to-insulator transition occurs at around 200 K due to the preferential dimerization of TCNQ$^{\cdot -}$ molecules (Epstein *et al.*, 1972; Coleman *et al.*, 1973). In order to maintain the metallic state down to low temperature and furthermore to achieve superconductivity, it is necessary to stabilize a uniform stacking structure of TCNQ$^{\cdot -}$ molecules. A possible approach for dimerization of TCNQ$^{\cdot -}$ molecules to be suppressed is to introduce sterically bulky substitutents on TCNQ$^{\cdot -}$ such as methyl groups and halogen atoms. In fact, for a tetramethyl-



(I)

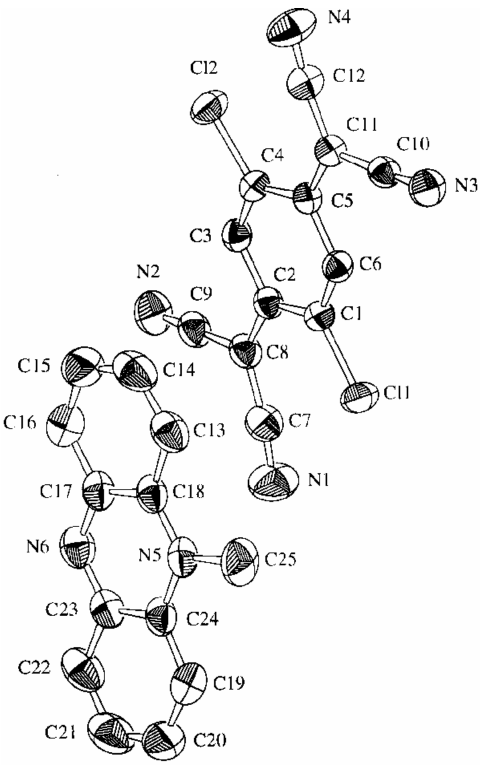


Figure 1
The molecular structure of (I) with ellipsoids plotted at the 50% probability level.

phosphonium ($\mathrm{PMe_4}^+$) salt of 2,5-dimethyl-substituted TCNQ radical anion ($\mathrm{Me_2TCNQ}^{\cdot -}$) and a tetramethylarsonium ($\mathrm{AsMe_4}^+$) salt of $\mathrm{Cl_2TCNQ}^{\cdot -}$ the $\mathrm{Me_2TCNQ}^{\cdot -}$ and $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecules form a uniform stacking structure at room temperature (Sugimoto *et al.*, 1998; Ueda *et al.*, 2001). In this paper, the structure of the title compound, $\mathrm{NMP}^+\cdot\mathrm{Cl_2TCNQ}^{\cdot -}$, (I), is reported.

The NMP^+ molecule shows high planarity (Fig. 1). On the other hand, the dihedral angles between the six-membered ring and two $\mathrm{C(CN)_2}$ groups in the $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecule are 3.0 (3) and 5.7 (4)°, which are slightly larger than those in $\mathrm{AsMe_4}^+\cdot\mathrm{Cl_2TCNQ}^{\cdot -}$ (Ueda *et al.*, 2001). Two of the four C—CN bonds are slightly bent which may occur to avoid the short C—N···Cl non-bonded interaction. This may be also the driving force of the non-planar structure of the $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecule.

As shown from the crystal structure viewed along the *a* and *b* axes in Fig. 2, columns of the NMP^+ and $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecules are alternately arranged along the *b* and *c* axes. The neighboring NMP^+ molecules related by a center of symmetry are dimerized with an interplanar distance of 3.42 (9) Å, which is comparable to a 'π-cloud thickness' (3.42 Å; Pauling, 1960). There is no overlap between the dimers, as is seen from the distance of 4.99 (2) Å between the centers of the pyrazine rings. On the other hand, the $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecules form a one-dimensional columnar structure along the *a* axis. The columnar structure is not uniform, and there are two kinds of modes (*A* and *B*) in the overlap of $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecules (Fig. 3). In the *A* mode, the neighboring molecules slip along the longer molecular axis to each other, and the centers of six-membered rings are separated by 2.14 (8) Å. This stacking mode is very similar to that of $\mathrm{TCNQ}^{\cdot -}$ molecules in $\mathrm{NMP}^+\cdot\mathrm{TCNQ}^{\cdot -}$, in which the distance between the centers of six-membered rings is 2.09 (4) Å (Fritchie, 1966). In the *B* mode, only the $\mathrm{C(CN)_2}$ groups of the neighboring molecules are overlapped with a large distance of 5.73 (1) Å between the centers of six-membered rings. The interplanar distances in the *A* and *B* modes are 3.11 (4) and 3.19 (2) Å, respectively, which are shorter than the 'π-cloud thickness.' As expected from such an irregular stacking of $\mathrm{Cl_2TCNQ}^{\cdot -}$ molecules, the title compound (I) exhibits very low electrical conductivity of 1×10^{-5} S cm^{-1} at room temperature.

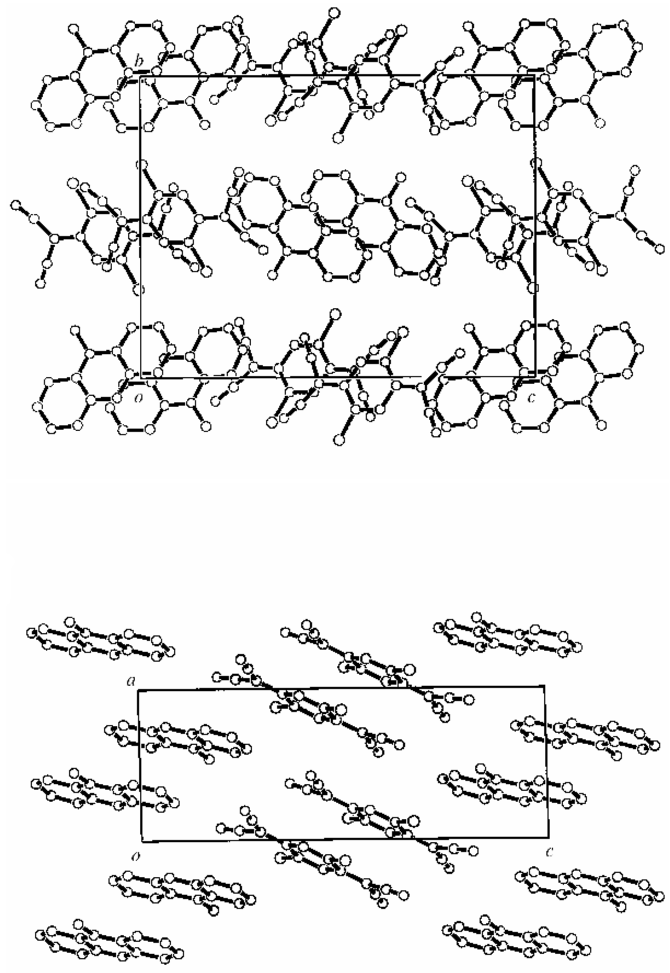


Figure 2
The crystal structure of (I) viewed along the a (top) and *b* (bottom) axes.

Experimental

Reaction of $\mathrm{Cl_2TCNQ}$ (Wheland & Martin, 1975; 43.8 mg, 0.604 mmol) with LiI (66.0 mg, 0.4931 mmol) in 2 ml of $\mathrm{CH_3CN}$ gave the Li^+ salt of $\mathrm{Cl_2TCNQ}^{\cdot -}$ (36.0 mg, 53% yield), followed by treatment with an equimolar amount of $\mathrm{NMP}^+\cdot\mathrm{CH_3OSO_3}^-$ (Kehrmann & Havas, 1913) in $\mathrm{H_2O}$ to afford the title compound, (I). Crystals of (I) were obtained from a $\mathrm{CH_3CN/Et_2O}$ solution (m.p. > 573 K).

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Crystal data

$C_{13}H_{11}N_2^+ \cdot C_{12}H_2Cl_2N_4^-$
$M_r = 468.32$
Monoclinic, $P2_1/c$
$a = 7.2978$ (3) Å
$b = 14.9895$ (5) Å
$c = 19.6091$ (6) Å
$\beta = 91.042$ (1)°
$V = 2144.7$ (1) Å^3
$Z = 4$

$D_x = 1.450$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15 754 reflections
$\theta = 2.9$–27.5°
$\mu = 0.33$ mm^{-1}
$T = 296$ K
Prism, purple
0.50 × 0.35 × 0.10 mm

Data collection

Rigaku RAXIS–RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan (*PROCESS-AUTO*; Rigaku Corporation, 1998)
$T_{\min} = 0.845$, $T_{\max} = 0.968$
19 531 measured reflections

4866 independent reflections
3415 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 27.5$°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.122$
$S = 1.32$
4866 reflections
298 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + \{0.05[{\rm Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C1	1.732 (2)	Cl2—C4	1.734 (2)
Cl1—C1—C2	120.9 (1)	N1—C7—C8	172.5 (3)
Cl1—C1—C6	117.0 (1)	N2—C9—C8	179.3 (2)
Cl2—C4—C3	117.2 (1)	N3—C10—C11	178.4 (2)
Cl2—C4—C5	120.6 (1)	N4—C12—C11	171.2 (2)

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: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

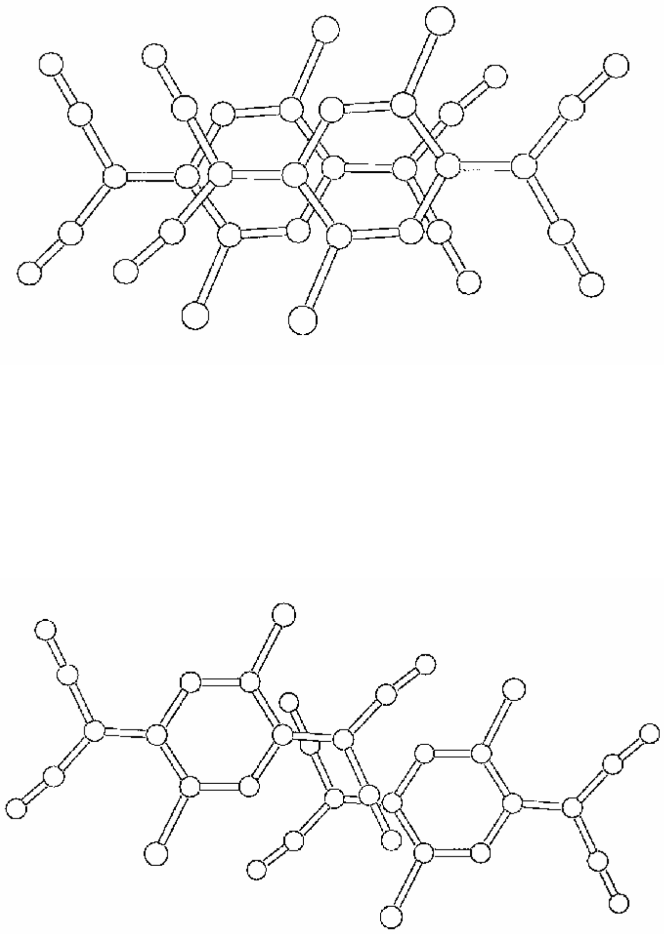

Figure 3
Two kinds of overlap modes, *A* (top) and *B* (bottom), within the Cl_2TCNQ^- column. The view direction is perpendicular to the molecular planes.

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