

The Crystal Structure of the Charge-Transfer Complex between *N*-Ethylphenazinium (EtP) and Dimerized 7,7,8,8-Tetracyanoquinodimethanide (TCNQ) Ions, $(C_{14}H_{13}N_2)_2 \cdot C_{24}H_8N_8^*$

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The title compound crystallizes in space group $P\bar{1}$ with $a = 7.7662$ (6), $b = 8.1151$ (12), $c = 16.397$ (2) Å, $\alpha = 87.21$ (1), $\beta = 93.61$ (1), $\gamma = 95.76$ (1)° and $Z = 1$. Two TCNQ ions are connected to form dimers by an unusually long 1.631 (5) Å σ -bond between two symmetry-related C(22) atoms (C to which the cyano groups are attached).

Introduction

Charge-transfer salts of 7,7,8,8-tetracyanoquinodimethanide, TCNQ, have been intensively studied in recent years primarily since their columnar structures result in highly anisotropic physical properties and occasionally very high, one-dimensional, room-temperature electrical conductivities. One of the first such organic 'metals' studied consisted of the 1:1 charge transfer compound with *N*-methylphenazinium (NMP) (Coleman, Cohen, Garito & Heeger, 1973). A new compound formed on substituting an ethyl for the methyl group drastically reduced (by over 11 orders of magnitude) the conductivity. This was particularly interesting since the unit-cell dimensions for this *N*-ethylphenazinium (EtP) compound appeared to suggest a doubling of the triclinic cell (Fritchie, 1966) of the highly conducting NMP analog. The structure determination described below proved a surprise for another reason; it revealed a new dimerized form of TCNQ radical anions unlike the π -bonded type previously reported (Herbstein, 1971; Ashwell, Eley, Fleming, Wallwork & Willis, 1976). These dimerized ions, $TCNQ_2^{2-}$, contain a long σ bond with a C–C distance of 1.631 Å. While preparing this manuscript

we learned of another structure determination in which such a dimer was found (Dong, Endres, Keller, Moroni & Nöthe, 1977).

Experimental details

Both the NMP and EtP compounds were prepared and crystallized by the method described by Melby (1965). Crystals of $(EtP)_2TCNQ_2$ are prismatic and appear blue-black upon reflection. On transmission, smaller single crystals are blue-green. Chemical analysis found 75.51, 4.12, 20.25% compared with 75.54, 4.12 and 20.34% for C, H and N, respectively. Precession and Weissenberg photographs were employed to determine the triclinic symmetry as well as to select a suitable specimen for data collection. The lattice constants given in the abstract were determined by least-squares fitting of the 2θ values for 30 strong hkl reflections between 43 and 55° 2θ with Mo $K\alpha$ ($\lambda = 0.710688$ Å) on a Picker diffractometer. The Mo $K\alpha$ intensity data were measured with a scintillation detector employing pulse-height discrimination, the θ – 2θ scan technique (to $2\theta = 55^\circ$) and a scan speed of 1° min^{-1} over the interval $2\theta_{\lambda_1} - 1.35^\circ$ to $2\theta_{\lambda_2} + 1.35^\circ$. There are 2726 observed and 1987 'less than' intensities. The 'less than' intensities were those for which the intensity value was less than 3σ , where $\sigma = (N_{sc} + K^2N_\beta)^{1/2}$ and N_{sc} , N_β ,

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Table 1. Atomic coordinates in $(EtP)_2 \cdot (TCNQ)_2$ ($\times 10^4$; for H $\times 10^3$)

	x	y	z		x	y	z
N(1)	-1460 (4)	1006 (3)	3045 (2)	C(22)	5846 (4)	256 (4)	304 (2)
N(8)	-1278 (4)	4457 (4)	3011 (2)	C(23)	3818 (4)	3835 (4)	3004 (2)
N(25)	2372 (5)	2320 (4)	4223 (2)	C(24)	3024 (4)	3004 (4)	3675 (2)
N(27)	4213 (6)	7004 (4)	2987 (2)	C(26)	4024 (5)	5584 (4)	2991 (2)
N(28)	8105 (4)	1971 (4)	-600 (2)	C(29)	6587 (4)	-1305 (4)	580 (2)
N(30)	7139 (4)	-2498 (4)	793 (2)	C(31)	-1576 (5)	-843 (4)	3058 (3)
C(2)	-740 (4)	1904 (4)	2405 (2)	C(32)	41 (7)	-1443 (6)	3487 (4)
C(3)	-46 (5)	1171 (5)	1746 (2)	H(3)	-5 (5)	11 (4)	172 (2)
C(4)	610 (5)	2158 (6)	1129 (2)	H(4)	103 (5)	163 (5)	71 (2)
C(5)	633 (5)	3888 (5)	1113 (2)	H(5)	111 (5)	445 (5)	67 (2)
C(6)	5 (5)	4627 (5)	1732 (2)	H(6)	6 (5)	569 (4)	175 (2)
C(7)	-691 (4)	3666 (4)	2408 (2)	H(10)	-262 (5)	-30 (4)	447 (2)
C(9)	-1906 (5)	3550 (4)	3648 (2)	H(11)	-365 (5)	126 (5)	549 (2)
C(10)	-2686 (5)	902 (5)	4386 (2)	H(12)	-360 (5)	406 (5)	538 (2)
C(11)	-3236 (5)	1775 (6)	4989 (2)	H(13)	-240 (5)	557 (5)	432 (2)
C(12)	-3155 (6)	3511 (6)	4952 (2)	H(16)	602 (4)	353 (4)	52 (2)
C(13)	-2514 (6)	4382 (5)	4306 (2)	H(17)	481 (4)	-84 (4)	179 (2)
C(14)	-2022 (4)	1779 (4)	3690 (2)	H(18)	516 (4)	494 (4)	166 (2)
C(15)	5428 (4)	1215 (4)	1034 (2)	H(19)	397 (4)	62 (4)	285 (2)
C(16)	5543 (4)	2946 (4)	1001 (2)	H(311)	-188 (5)	-115 (5)	246 (2)
C(17)	4846 (4)	362 (4)	1741 (2)	H(312)	-270 (5)	-125 (5)	326 (2)
C(18)	5043 (4)	3794 (4)	1642 (2)	H(321)	3 (5)	-260 (5)	339 (2)
C(19)	4345 (4)	1208 (4)	2379 (2)	H(322)	8 (6)	-113 (6)	401 (3)
C(20)	4403 (4)	2950 (4)	2347 (2)	H(323)	95 (6)	-103 (5)	312 (3)
C(21)	7131 (4)	1232 (4)	-203 (2)				

and K are the total scan count, background counts and the time ratio of the scan to background, respectively. The observed density of 1.33 g cm^{-3} (Melby, 1965) may be compared with 1.338 g cm^{-3} calculated with $Z = 1$ and a FW of $(C_{14}H_{13}N_2)_2 \cdot C_{24}H_8N_8$, i.e. 2 EtP and 1 dimerized TCNQ ions. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962), those for H from Stewart, Davidson & Simpson (1965).

In the course of solving this structure, direct methods were applied unsuccessfully. In retrospect it was found that the eight highest E value reflections (corresponding to 2^5 possible structures) would give correct phases for the 52 next highest E value reflections, which, in turn, will generate 648 phases for reflections with E values greater than 1.35. The Fourier map from these 648 reflections shows only two thirds of the heavy atoms; there are 7 extraneous peaks higher than 10 of the true peaks and 10 more correct peaks missing among the highest 35. In addition, the peak values were spread over a rather large range. The method used in the final solution described below should have been applied to the E maps. Careful plotting, rather than reliance on computer searching, would have revealed two thirds of the structure.

The actual solution was obtained by using $P1$ rather than $P\bar{1}$ symmetry and by using a phenazinium ring plus a benzene ring situated to be compatible with the Patterson map; two sets of ghost peaks were noted. Either set could define the origin for the $P\bar{1}$ model.

The more reasonable set based on interatomic separations yielded a model which progressed from a value for R of 0.70 to the final solution ($R = 0.063$). This approach was almost abandoned when it became apparent that the TCNQ were too close together; however, the systematic reduction of the value of R was considered to be of more importance and this led to the correct solution. In the latter stages, H positions were obtained from a difference Fourier synthesis and these were assigned the isotropic thermal parameters of the C atoms to which they are bonded. Then these H positions with fixed thermal parameters together with anisotropic parameters for the heavy atoms were subjected to further least-squares refinement. The function $w(F_o - F_c)^2$ was minimized with $w = 1/\sigma^2$. A value of R equal to 0.063 was obtained.* The final positional parameters are given in Table 1 with the labeling scheme shown in Fig. 1. The H atoms are labeled with the same number (plus an additional digit on the aliphatic C) as the C atom to which they are bonded. Bond lengths and angles are shown in Fig. 2. The final computations were performed with the XRAY 76 system (Stewart, 1976).

* A list of structure factors, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32999 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

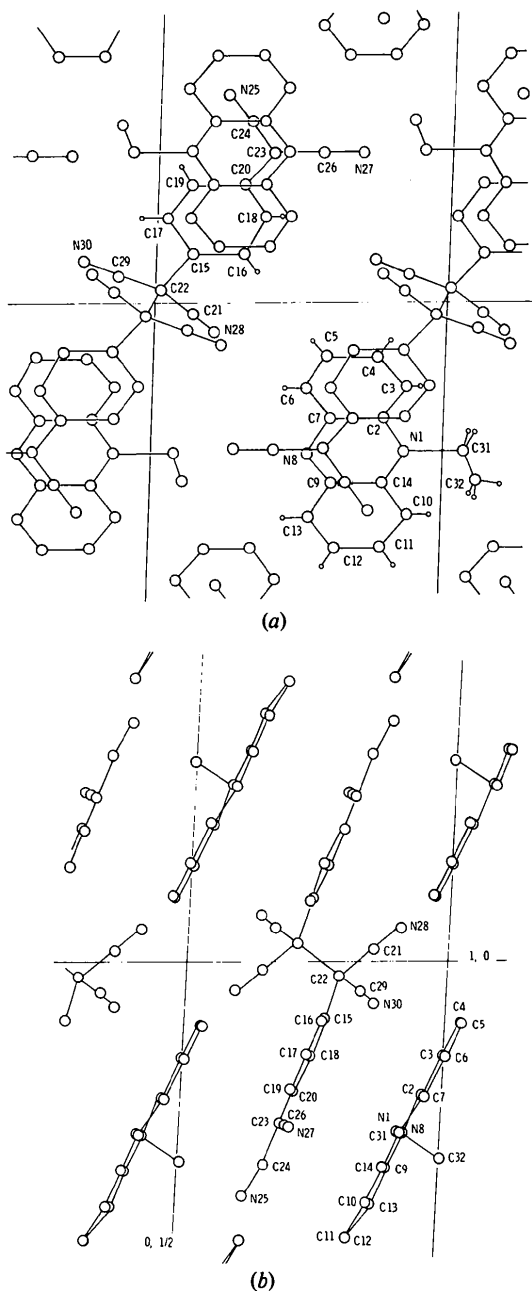


Fig. 1. (a) Projection along [100] in $(\text{EtP})_2 \cdot \text{TCNQ}_2$. The labeling scheme employed in this communication is shown. A symmetry-related EtP ion is labeled so as to avoid clutter. Hydrogen atoms are shown only on labeled portions of the figure. Overlapping of the π -electron system of the EtP ion with the aromatic portion of the TCNQ dimer involves 3.29 Å separations; the closest interatomic distance for the aliphatic tail is 3.34 Å for N(28)–C(4). The shortest contact perpendicular to such stacks is a 3.34 Å [C(17)–N(27')] separation along [010]. Other heavy-atom contacts exceed 3.40 Å. (b) Projection along [010]. This edge-on view shows the stacking of the dimer ions in nearly parallel orientation with respect to the two EtP ions. The least-squares plane through the ring atoms of the TCNQ and that through the EtP ion form an angle of only 3.5°.

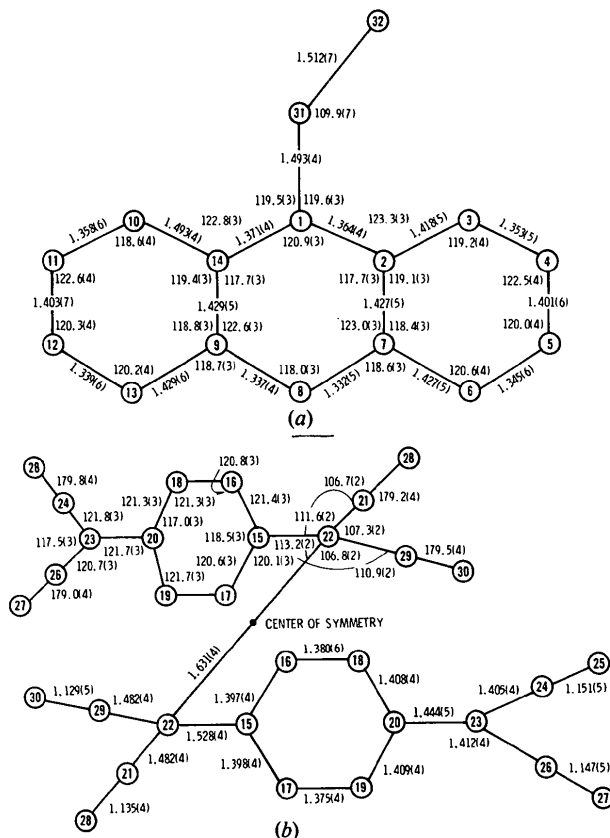


Fig. 2. (a) Bond lengths and angles for the EtP ion. The refined hydrogen positions yield ring C–H distances from 0.87 to 0.99 (4) Å and aliphatic C–H distances from 0.95–1.03 (4) Å. (b) Bond lengths and angles for the TCNQ dimer ions. Note the differences in length about the aliphatic C(22) and aromatic C(23) ends of this ion as well as the corresponding C–N distances. The C–H distances range from 0.93 to 0.99 (4) Å.

Discussion

The unique combination of the donor–acceptor mixed stacks and the σ -bond dimerization of the TCNQ ions is consistent with the low value of the conductivity of this material [single-crystal, room-temperature conductivity $\sim 10^{-9}$ ($\Omega \text{ cm}$) $^{-1}$ (Melby, 1965)] compared with the methyl analog NMP–TCNQ [single-crystal, room-temperature conductivity 380 ($\Omega \text{ cm}$) $^{-1}$ (Coleman, Cohen, Garito & Heeger, 1973)]. The many charge-transfer salts of TCNQ with mixed-stack structures have conductivities between 10^{-5} and 10^{-9} ($\Omega \text{ cm}$) $^{-1}$, while those with separate, but non-uniform (dimers, trimers, and tetramers) TCNQ stacks have conductivities between 10^{-2} and 10^{-5} ($\Omega \text{ cm}$) $^{-1}$. In NMP–TCNQ, stacks of the identical ions formed columns parallel to c , whereas in this compound the complex column consists of alternate ions, one TCNQ_2^{2-} ion with two parallel EtP^+ ions, but at slightly different elevations to conform with the two different parts of the TCNQ_2^{2-} ion. The least-squares plane through the ring

atoms of the TCNQ and that through the EtP ion form an angle of 3.5° ; hence, the alternate ions are essentially parallel. The EtP ion tends to be slightly bowed with the two least-squares planes through the two sets of six C and two N atoms forming an angle of 2.1° .

The EtP⁺ ions are aromatic, as evidenced by the values of the N—C distances. The N—C lengths on the hydrogen side of the cation are similar to values found in analogs with aromatic character [1.338 (5) and 1.349 (4) Å in α -phenazine-TCNQ (Goldberg & Shmueli, 1973b); 1.336 (8) and 1.333 (7) Å in (NMP)₂(TCNQ)₃ (Sanz & Daly, 1975)] and those on the ethyl side are shorter than those of the 15π -electron aliphatic dimethyl analog [values of 1.383 (4) and 1.389 (4) Å (Goldberg & Shmueli, 1973a)] and similar to the 1.373 (7) and 1.368 (7) Å values in (NMP)₂(TCNQ)₃ (Sanz & Daly, 1975).

The most interesting feature of this structure consists of the TCNQ₂²⁻ ion. Dimerization occurs *via* an unusually long 1.631 (5) Å C—C bond between C(22) and C(22') (this bond is situated at an inversion center). Hence, C(22) is essentially tetrahedral. The loss of aromaticity of this portion of the ion is further evidenced by the longer C(22)—C(21) and C(22)—C(29) and shorter cyano distances (Fig. 2). The separations and angles in the dimer are in good agreement with values obtained by Dong, Endres, Keller, Moroni & Nöthe (1977) in the bis(dipyridyl)platinum(II)-TCNQ₂ compound. Gas-phase electron diffraction on highly crowded molecules has given long C—C bond distances which approach our value; for example 1.611 (5) Å is found in tri-*tert*-butylmethane (Bürgi & Bartell, 1972).

It is interesting to compare the arrangement of the TCNQ radical ions in (NMP)₂(TCNQ)₃ with that in our material. In that compound (Sanz & Daly, 1975), trimers exist in which a central TCNQ is closely π -bonded (separations of 3.14 Å) to two other symmetry-related TCNQ radical ions. Of particular interest are the overlaps of adjacent trimers; these involve a separation near 3.35 Å, with an arrangement in which the closest atomic contacts between TCNQ ions involve the methylene C. Should this distance be shortened,

through a pressure or temperature change, a σ bond could form, resulting in a dimer arrangement similar to that observed in our compound. The overlap of the opposite tail of the TCNQ with the NMP ion also involves an arrangement similar to that between the EtP and TCNQ₂ groups in our material.

Crystals of (EtP)₂TCNQ₂ have been examined optically at higher temperatures in order to observe any color change which might be associated with the σ bond breaking, with the formation of the normal planar geometry for TCNQ ions. However, no change was seen before the material decomposed.

The question concerning the chemistry of TCNQ radical ions remains. At this time, we are unable to explain the formation of the σ -bond dimer in this material, as opposed to the usual donor-acceptor stack or π -bond dimer structures.

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