Crystalline and molecular structure of novel anion-radical salt (N–Et–Pz)(TCNQ)$_3$
(Pz is pyrazine)

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Crystalline and molecular structure of previously synthesized by the authors anion-radical salt (ARS) 7,7,8,8-tetracyanoquinodimethane (TCNQ) of an unusual \([N-(H_2C=)-Pz]_3\) (TCNQ)$_3$ composition (where Pz is pyrazine) has been determined. The structure of the given ARS is also unusual because unlike most of structures known it consists of bulk formed by two A and C TCNQ types, particles of the third B type being located at the angle of 117.7 and respectively 117.4 degrees relatively to them. C type particles interact appreciable with pyrazine cations through pyrazine non-alkylated nitrogen atom. B-type particles as well as TCNQ particles in columns, possess an appreciable charge (about \(-0.3\)). Such a peculiarity of structure renders ARS electronic system some what two-dimensional that is unusual for TCNQ ARS and agrees with the electrophysical measurements.

Определена кристаллическая и молекулярная структура синтезированной ранее авторами анион-радикальной соли (АРС) 7,7,8,8-тетрацианоанилинодиметана (TCNQ) необычного состава \([N-(\text{H}_2\text{C}=)\text{-Pz}]_3\) (TCNQ)$_3$, где Pz — пиразин. Структура данной ARS также необычна — в отличие от большинства известных структур, она состоит из столбов, образованных двумя типами TCNQ — А и С, перпендикулярно которым расположены частицы третьего типа — В. Частицы типа С заметно взаимодействуют с кационами пиразина посредством неалкилированного атома азота пиразина. Частицы типа B, как и частицы TCNQ в столбках, обладают заметным зарядом (около \(-0.3\)). Такая особенность структуры придает электронной системе ARS определенную двумерность, необычную для ARS TCNQ, и согласуется с результатами электрофизических измерений.

TCNQ based ARS gave impetus to the researches late in sixties in view of the problem of high-temperature superconductivity based on Little model [1, 2]. ARS of NMP-TCNQ (NMP—N-methylphenazine-ion) was one of the first organic metals in which however transition to the state of Mott’s dielectric when \(T_M \approx 220\) K was observed [2]. After the discovery of organic metals and subsequently of superconductors based on cation-radical salts (CRS) of tetraethalvalene and its derivatives [8] the interest to ARS of TCNQ becomes less. However, after the discovery of melting conducting organic materials based on ARS of TCNQ [4, 5], the interest to them is increased again. Such compounds may be employed in the develop-
ment of a new type electrolyte metaloxide

capacitors [6, 7], that possess high oper-

tional characteristics, namely, the ability to

"self-treatment" of oxide layer defects [8].

Electrophysical and optical researches of

melting conducting ARS of TCNQ carried

by us both in solid and in melts [9], has

every reason to suppose that ARS melt of

TCNQ [9] can behave as a conducting liquid

crystal, in which the column structure,

characteristic of all TCNQ based conducting

compounds is maintained. The presence of

ARS of TCNQ that are ferromagnetic ordered

at room temperature [10] is a strong evidence

that these salts are much promising.

ARS TCNQ with N-alkylpyrazinium cat-

ions have a particular interest, because of

pyrazine is a simplest analog of phenazine,

and based on the last, the first organic

metal had been made. Possessing such a

nonalkylated nitrogen atom such a cation

may interact quite specifically with TCNQ-

anion-radicals or with donor-acceptor inter-

action of metal cations, that may result in

the formation of supramolecular structures.

We have synthesized simple and complex

conducting TCNQ and MeTCNQ salts with

pyrazine-based cations [11, 14]. Like ARS

NMP–TCNQ of salt of a simple [N–(H$_3$C)–

Pz]2[TCNQ] composition is also an organic

metal, in which a metallic state is stable
down to 120 K. This seems to be an ex-

treemly low metal-dielectric transition tem-

perature for ARS of TCNQ with cations of

a "closed" type.

Synthesis, crystalline and molecular struc-

ture, optical and electrophysical proper-

ties of the novel ARS of unusual composi-

tion [N–(H$_3$C)–Pz]2(NEPz–(TCNQ)$_3$)2

are described in this article. This ARS is

the first example of TCNQ salt with quasi-

two-dimensional electronic structure, unlike
general quasi-one-dimensional ARS TCNQ

structure.

Aldrich firm pyrazine was used in the

experiment; TCNQ was purified by method

of vacuum zone sublimation; ethylidiole

was synthesized according to the reaction of

ethanol with phosphorus triiodide followed

by distillation in the inert atmosphere.

N-ethylpyrazinium iodide was prepared by

reaction:

$$\text{Pz + EtI} \rightarrow (\text{NEPz})_2.$$  

NEPz–(TCNQ)$_3$ ARS was obtained by:

1.5(NEPz)$_2$ + 3TCNQ →

→ NEPz – (TCNQ)$_3$ + 0.5(NEPz)$_2$.

ARS precipitate was filtered, washed

with ether and hexane and dried under vac-

uum. In order to grow single crystals and

for purification recrystallization from ace-

tone was used. Black-violet needle crystals

with length up to 3 mm had been obtained.

ARS composition was determined spectro-

photommetrically in acetonitrile by measur-

ing optical density both at 394 nm, where

anion-radicals as well as TCNQ molecule ab-

sorb, and at 840 nm, where anion-radicals

only absorb. Composition of salt in aceton-

itrile solution may be determined by the rela-

tion:

$$\frac{[\text{TCNQ}]}{[\text{TCNQ}^2]} = 0.74 \frac{D_{394}}{D_{840}} - 0.35,$$

where $D_\lambda$ — optical density on the respec-

tive wavelength.

$$C_{02}H_2N_4, M = 721.72 \text{ g/mol; monoclinic, space group C2/m, Z} = 4, a = 3699.8(7),$$

$$b = 1264.0(3), c = 656.80(33) \text{ pm, } \alpha = 90,$$

$$\beta = 91.24(3), \gamma = 90 \text{ deg, } V = 3070.8(1) 10^6 \text{ pm}^3,\text{ Mo-K}_\alpha, T = 293(2) \text{ K.}$$. A difractometer

STOE STADI4 with flat detector had been used

do find data collecting. 5028 independent

reflections ($R_{IJ} = 0.1267$) were chosen from

9380 ones. The structure was determined by
direct (SHELXS-97) method and refined by

full-matrix method of least-squares for $P^2$

in anisotropic approximation [12]. The non-

hydrogen atoms were refined anisotropi-

cally, while the hydrogen atoms were intro-
duced geometrically and refined according a

"rider" model with $U_{iso} = 1.2U_{eqw}$ of the

respective carbon atom. Largest diffusion

peak and hole: 0.246 and $-0.227 \text{ e}/\text{Å}^3$, 275

parameters, all heavy atoms being anisot-

ropic. Final validation data are: $R1$ and $wR2$

values were 0.0767 [$U > 2\sigma(I)$] and 0.1877

respectively along the whole range of inde-

pended reflections; $S < 1.00$. The weight-
ing function used was $w = 4F^2_0/\sigma^2 (F^2_0)$

for the function of $\sum \sigma (F^0_0 - |F^c|)^2$ to be mini-

mized. The ORTEP drawings, and full tables of fractional atomic coordinates and in-
teratomic bond distances, have been depos-
ited at the Cambridge Crystallographic Data

Centre, supplementary publications No.221851. Bond lengths and valence angles are

listed in Tables 1 and 2, enumeration of atoms is shown on Fig. 1. Fig. 2 shows the

structure projection along the direction [100].

Synthesized compound was investigated by two experimental techniques: measurement

of their absorption in the infrared (IR) spectral range and studies of the elec-
### Table 1. Bond’s lengths (pm) in the ARS NEPz–(TCNO)$_3$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)–N(1)</td>
<td>114.1(5)</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>141.6(5)</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>138.3(7)</td>
</tr>
<tr>
<td>C(2)–C(1)#1</td>
<td>141.6(5)</td>
</tr>
<tr>
<td>C(3)–C(4)</td>
<td>144.0(4)</td>
</tr>
<tr>
<td>C(4)–C(5)</td>
<td>134.6(5)</td>
</tr>
<tr>
<td>C(5)–C(6)</td>
<td>143.8(4)</td>
</tr>
<tr>
<td>C(6)–C(7)</td>
<td>138.9(7)</td>
</tr>
<tr>
<td>C(7)–C(8)</td>
<td>143.3(4)</td>
</tr>
<tr>
<td>C(8)–N(2)</td>
<td>114.8(6)</td>
</tr>
<tr>
<td>C(9)–N(3)</td>
<td>112.9(6)</td>
</tr>
<tr>
<td>C(9)–C(10)</td>
<td>143.7(6)</td>
</tr>
<tr>
<td>C(10)–C(11)</td>
<td>137.6(8)</td>
</tr>
<tr>
<td>C(10)–C(9)#2</td>
<td>143.7(6)</td>
</tr>
<tr>
<td>C(11)–C(12)</td>
<td>143.1(5)</td>
</tr>
<tr>
<td>N(6)–C(21)#1</td>
<td>134.7(9)</td>
</tr>
<tr>
<td>N(7)–C(22)#1</td>
<td>134.7(9)</td>
</tr>
</tbody>
</table>

### Table 2. Valence angles (degree) in the ARS NEPz–(TCNO)$_3$

<table>
<thead>
<tr>
<th>Angle</th>
<th>Value (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)–C(1)–C(2)</td>
<td>177.5(5)</td>
</tr>
<tr>
<td>C(3)–C(2)–C(1)</td>
<td>122.6(2)</td>
</tr>
<tr>
<td>C(3)–C(2)–C(1)#1</td>
<td>122.6(2)</td>
</tr>
<tr>
<td>C(3)–C(2)–C(1)#1</td>
<td>114.8(5)</td>
</tr>
<tr>
<td>C(2)–C(3)–C(4)</td>
<td>121.4(2)</td>
</tr>
<tr>
<td>C(4)–C(3)–C(4)</td>
<td>117.2(5)</td>
</tr>
<tr>
<td>C(5)–C(4)–C(3)</td>
<td>121.6(4)</td>
</tr>
<tr>
<td>C(4)–C(5)–C(6)</td>
<td>120.2(5)</td>
</tr>
<tr>
<td>C(7)–C(6)–C(5)</td>
<td>120.5(2)</td>
</tr>
<tr>
<td>C(7)–C(6)–C(5)#1</td>
<td>120.5(2)</td>
</tr>
<tr>
<td>C(5)–C(6)–C(5)#1</td>
<td>119.0(5)</td>
</tr>
<tr>
<td>C(8)–C(7)–C(6)</td>
<td>122.9(2)</td>
</tr>
<tr>
<td>C(8)–C(7)–C(6)#1</td>
<td>114.3(5)</td>
</tr>
<tr>
<td>N(2)–C(8)–C(7)</td>
<td>178.0(5)</td>
</tr>
<tr>
<td>N(3)–C(9)–C(10)</td>
<td>174.8(6)</td>
</tr>
<tr>
<td>N(10)–C(10)–C(9)</td>
<td>123.3(3)</td>
</tr>
<tr>
<td>C(11)–C(10)–C(9)</td>
<td>123.3(3)</td>
</tr>
<tr>
<td>C(9)–C(10)–C(9)#2</td>
<td>113.8(6)</td>
</tr>
<tr>
<td>C(10)–C(11)–C(12)</td>
<td>120.7(3)</td>
</tr>
<tr>
<td>C(12)–C(11)–C(10)#2</td>
<td>118.7(6)</td>
</tr>
<tr>
<td>C(12)#1–C(12)–C(11)</td>
<td>120.7(3)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 x, -y + 1, z; #2 -x, y, -z + 1.
electric conductivity of the obtained samples. In the studies of IR absorption spectra a technique of pelleting with KBr was applied, with registration at room temperatures on the Specord-75 IR spectrophotometer, wave numbers ranging from 400 to 4000 cm⁻¹. DC current electric conductivity of single crystals of the synthesized salt has been measured in the temperature range of 77–300 K by the scheme of four-point connection of the studied sample.

As Fig. 2 shows, ARS structure is built by alternated TCNO columns (molecules A and C types), whose planes are almost parallel (dihedral angle is 0.3 degree), interplanar distance in columns are 3.25 and 3.32 Å. B molecules are located at the angle of 117.7 and respectively 117.4 degrees relatively to them. N-ethylpyrazinium is oriented relatively to C molecules in such a way, that free nitrogen atom of pyrazine is located between two nitrile groups of C molecule.

It's important to know the charge distribution in given ARS (one electron is divided into three TCNO particles) in order to interpret the results of electrophysical measurements. As the degree of quinoidity decreases when electron is added to the TCNO molecule, the latter is in a definite dependence upon TCNO charge. The degree of quinoidity may be determined with bond lengths in TCNO molecule by energy of stabilization calculation in the framework of harmonic oscillator model — HOSE (Harmonic Oscillator Stabilization Energy) [13]. As shown elsewhere [13], the value of quinoidity is linearly dependent upon TCNO charge with correlation coefficient of $r = 0.992$. Proceeding from the data in Table 1, we calculated HOSE energies for quinoid and Kekule's TCNO structures for A, B and C particles and their charges (see Table 3).
Table 3. HOSE model data (kJ/mol) for a three TCNO species in NEpZ–(TCNQ)$_3$ ARS and Flandrois&Chasseau charge $Q$

<table>
<thead>
<tr>
<th>Species</th>
<th>HOSE$_1$</th>
<th>% Quinoidity</th>
<th>HOSE$_2$</th>
<th>% Kekule’s structure</th>
<th>HOSE$_{tot}$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.17</td>
<td>86.6</td>
<td>79.71</td>
<td>13.5</td>
<td>16.03</td>
<td>0.10</td>
</tr>
<tr>
<td>B</td>
<td>11.19</td>
<td>77.1</td>
<td>75.18</td>
<td>22.9</td>
<td>25.88</td>
<td>0.31</td>
</tr>
<tr>
<td>C</td>
<td>17.00</td>
<td>65.4</td>
<td>64.40</td>
<td>34.5</td>
<td>33.39</td>
<td>0.56</td>
</tr>
</tbody>
</table>

$$R(T) = A \exp \left[ \frac{1}{T} \left( \frac{T_0}{T} \right)^{\alpha - 1} \right]$$

Here $\alpha$ is the dimensionality of the system, $T_0$ and $A$ are the parameters of the model.

For the NEpZ–(TCNQ)$_3$ compound best fit of the experimental and theoretical $R(T)$ dependencies occurs for $\alpha = 2$, which corresponds to two-dimensional case. Logarithm of the reduced electric resistance $R/R_{RT}$ is expressed as:

$$\ln \left( \frac{R}{R_{RT}} \right) = -21.85 + \frac{175.20}{T^{1/2}}$$

Thus, results of resistive measurements confirm essentially quasi-two-dimensional conductivity character of this ARS following from features of its crystal structure.

Thus, the unusual crystalline structure of a complex salt of 1:3 composition is determined for the first time for ARS of TCNQ as well as possibility of preparation of TCNQ based quasi-two-dimensional organic conductive materials is shown, which agrees with studied electrophysical properties of a given ARS quite well.

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References

Кристалічна та молекулярна структура нової аніон-радикальної солі (N-Et-Pz)(TCNQ)$_3$
(Pz - піразин)

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Визначено кристалічну і молекулярну структуру синтезованої авторами раніше аніон-радикальної солі (APC) 7,7,8,8-тетрацианофенанілметану (TCNQ) незвичайного складу $\left[N-(H_5C_2)-Pz\right](TCNQ)_3$, де Pz — піразин. Структура даної APC також незвичайна — на відміну від більшості відомих структур, вона складається зі стопок, утворених двома типами TCNQ — $A$ та $C$, перпендикулярно яким розташовані частки третього типу — $B$. Частки типу $C$ помітно взаємодіють з катіонами піразину за допомогою неполяризованого атому азоту піразину. Частки типу $B$, як і частки TCNQ у стопках, мають помітний захід (близько $-0.3$). Така особливість структури додає електронній системі APC нову двохрізь, незвичайну для APC TCNQ, і добре узгоджується з результатами електрофізичних вимірів.