

**New anion-radical salts
(N-Me-2,5-di-MePz)(TCNQ)₂ and
(N-Me-2,6-di-MePz)(TCNQ)₂ (Pz is pyrazine)**

O.N.Kazheva, D.V.Ziolkovskiy^{}, G.G.Alexandrov^{**},
O.A.Dyachenko, V.A.Starodub^{****}, A.V.Khotkevich^{***},
G.Y.Vasilets^{*}*

Institute of Chemical Physics Problems, Russian Academy of Sciences,
1 Semenov Ave., 142432 Chernogolovka, Russia

^{*}V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

^{**}N.Kurnakov Institute of General and Inorganic Chemistry, Russian
Academy of Sciences, 31 Leninsky Ave., 119991 Moscow, Russia

^{***}B.Verkin Institute of Low Temperature Physics and Engineering,
National Academy of Sciences of Ukraine,
47 Lenin Ave., 61108 Kharkiv, Ukraine

^{****}Institute of Chemistry, Jan Kichanowski University,
5 Chencinska str., 25-020 Kielce, Poland

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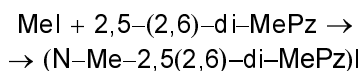
Anion-radical salts (ARS) of 7,7,8,8-tetracyanoquinodimethane (TCNQ) containing N-methyl-2,5-dimethyl-pyrazinium (N-Me-2,5-di-Me-Pz)⁺ and N-methyl-2,6-dimethyl-pyrazinium (N-Me-2,6-di-Me-Pz)⁺ cations have been first synthesized. Their X-ray structure analysis has been performed, crystal and molecular structures have been determined, IR spectra have been investigated and electroconductive properties have been studied in a wide temperature range.

Впервые получены анион-радикальные соли 7,7,8,8-тетрацианохинодиметана (TCNQ) с катионами N-метил-2,5-диметилпиразиния (N-Me-2,5-di-Me-Pz)⁺ и N-метил-2,6-диметилпиразиния (N-Me-2,6-di-Me-Pz)⁺. Проведен РСА монокристаллов, определены молекулярная и кристаллическая структура, изучены ИК-спектры и электропроводность в широком диапазоне температур.

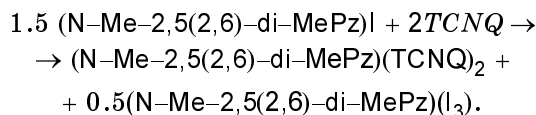
Anion-radical salts (ARS) of 7,7,8,8-tetracyanoquinodimethane (TCNQ) were the first organic objects to exhibit metallic properties [1]. In the middle 80s, conducting ARS of TCNQ were synthesized possessing a unique ability to melt without decomposition [2, 3]. This reveals wide usage possibilities of such ARS in electronic techniques. TCNQ ARS with cations containing an additional donor atom (for instance, cations pyrazine-based), can be used to deposit conducting

organic coatings over a metallic substrate. In these ARS, there is a possibility of additional interactions (besides electrostatic ones) between anion-radical TCNQ stacks and cations via non-alkylated nitrogen atom of pyrazine. This may result in structures unusual for TCNQ ARS. Using this approach, we have synthesized for the first time the quasi-two-dimensional TCNQ ARS of (N-Et-Pz)(TCNQ)₃ [4], (N-Et-2,5-di-Me-Pz)(TCNQ)₂ [5] composition and (N-Me-NH₂-Pz)(TCNQ)₂

with dimeric cation [6]. It is well known [7] that the increase of the system dimensionality stabilizes metallic state in low-dimensional conducting materials, the suppressing Pierls instability. In this connection, works in the field are of undoubted interest. In this work, we describe synthesis, crystal and molecular structure, electroconductive properties and IR spectra of new ARSs with cations based on pyrazine derivatives-2,5-dimethyl-pyrazine (2,5-di-Me-Pz) and 2,6-dimethylpyrazine (2,6-di-Me-Pz). 2,5-dimethylpyrazine and 2,6-dimethylpyrazine from Aldrich were used in the experiment; TCNQ was purified by vacuum zone sublimation; methyl iodide was synthesized by reacting methanol with phosphorus triiodide followed by distillation in an inert atmosphere. N-methyl-2,5-dimethyl- and N-methyl-2,6-di-methyl-pyrazinium iodides were prepared using reaction:



(N-Me-2,6-di-MePz)(TCNQ)₂ and (N-Me-2,5-di-MePz)(TCNQ)₂ ARS were obtained in the following manner:



The ARS precipitates were filtered, washed with ether and hexane and dried in vacuum. In order to grow single crystals and for purification, recrystallization from acetonitrile and acetone was used. Black-violet needle crystals of up to 25 mm length and hexagonal plates of up to 4 mm width had been obtained for (N-Me-2,5-di-MePz)(TCNQ)₂ (I) and (N-Me-2,6-di-MePz)(TCNQ)₂ (II), respectively. The ARS composition was determined using spectrophotometry, as described in [4, 5].

X-ray diffraction experiments on (I) and (II) crystals were performed using an Enraf Nonius CAD-4 diffractometer ($\omega/2\theta$ -scanning, Mo-K α radiation, graphite monochromator). The crystal structures were solved by direct methods and following Fourier synthesis using the SHELXS-97 software [8]. The structures were refined by full-matrix least squares procedures using an anisotropic approximation for all non-hydrogen atoms within the SHELXS-97 program [9]. Hydrogen atoms in (I) were calculated; in (II), found experimentally and refined isotropically.

Table 1. Crystal data for [N-Me-2,5-di-Me-Pz](TCNQ)₂ (I) and (N-Me-2,6-di-Me-Pz)(TCNQ)₂ (II).

Compound	(I)	(II)
Chemical formula	C ₃₁ H ₁₉ N ₁₀	C ₃₁ H ₁₉ N ₁₀
Chemical formula weight	531.56	531.56
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
Temperature, K	293	293
<i>a</i> /Å	7.218(1)	6.523(2)
<i>b</i> /Å	7.909(2)	7.653(2)
<i>c</i> /Å	13.433(3)	27.992(7)
α /°	81.30(3)	87.43(2)
β /°	84.27(3)	85.13(2)
γ /°	65.36(3)	78.62(2)
<i>U</i> /Å ³	688.4(2)	1364.4(6)
<i>Z</i>	1	2
λ /Å	0.7107	0.7107
<i>D</i> _{calc} /g·cm ⁻³	1.28	1.29
μ /mm ⁻¹	0.082	0.083
Number of measured reflections	3177	4228
Number of independent reflections	2410	4228
Number of observed reflections ($F_0 \geq 4\sigma(F_0)$)	1221	1869
Parameters refined	203	427
<i>R</i>	0.056	0.035
$(2\theta)_{max}$, °	49.96	47.98
Interval for <i>h</i>	-8 ≤ <i>h</i> ≤ 2	0 ≤ <i>h</i> ≤ 7

In the cation of (I) C(3)H₃ methyl group bound with N(1) atom is transformed into C(3a)H₃ group at N(1a) atom according to crystallographic symmetry conditions, with positions occupations equal to 0.5. Thus, in the cation layer of (I), cations of two types are present in equal amounts and distinguished by position of CH₃-derivatives at the nitrogen atom. The main crystallographic data of the compounds are listed in Table 1.

The synthesized compounds were investigated by two experimental techniques: IR absorption measurement and electric conductivity studies. To measure the IR absorption spectra, the pelleting technique with KBr was applied, with registration at room temperature

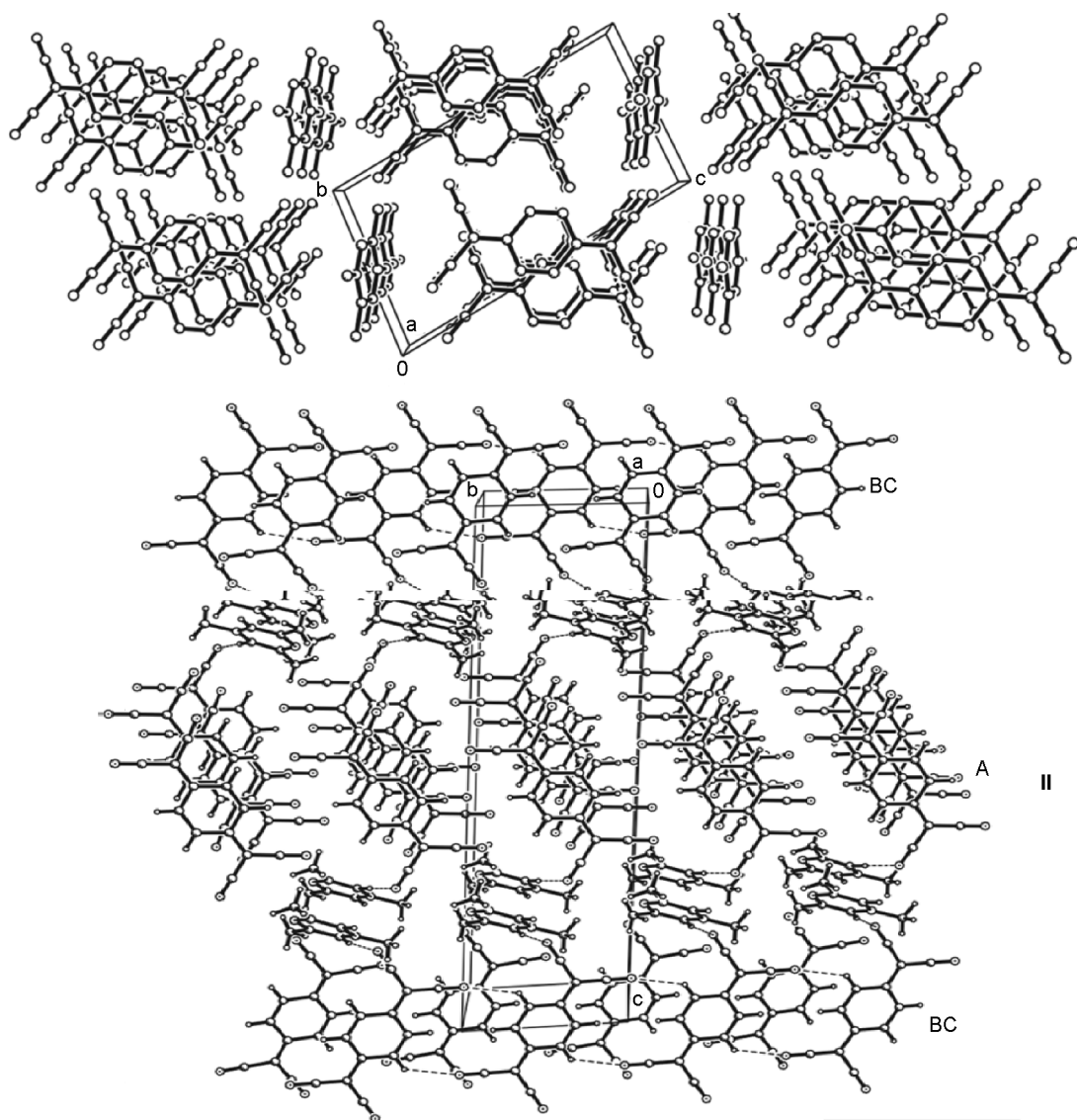


Fig. 1. Fragments of crystal structure of (I) and (II).

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 salts was measured in the 77–300 K temperature range using the four-point connection scheme.

The crystal structure of (I) is formed by N-methyl-2,5-dimethylpyrazinium $[\text{N-Me-2,5-di-Me-Pz}]^+$ cation in a special position and TCNQ anion in general position. The salt has a layered structure (Fig. 1), where cation layers alternate along the c axis with TCNQ layers. Anions in (I) form stacks along the a axis, where they are situated in pairs shifted with respect to each other, and characterized by two overlapping manners (Fig. 2). Within the pairs, molecules are eclipsed to a higher degree (Fig. 2a) than between the pairs (Fig. 2b). That is why we

can suggest the TCNQ dimerization in stacks, despite the fact that interplanar distances within and between the pairs are essentially the same (3.24 and 3.27 Å, respectively). Cation and anion in (I) are practically planar, the maximum deviation making 0.01 Å (C(9) atom). Basing on bond lengths (Table 2), we have estimated the TCNQ charge, using the same method as in [4]. According to these data the TCNQ particles in I have a charge of -0.44 .

The crystal structure of (II) is formed by $[\text{N-Me-2,6-di-Me-Pz}]^+$ cation situated in general position and three TCNQ anions (A, B, C), one of which (A) takes a general position and B and C anions are situated in special center-symmetrical positions. The X-ray structure analysis has revealed that salt (II) has a

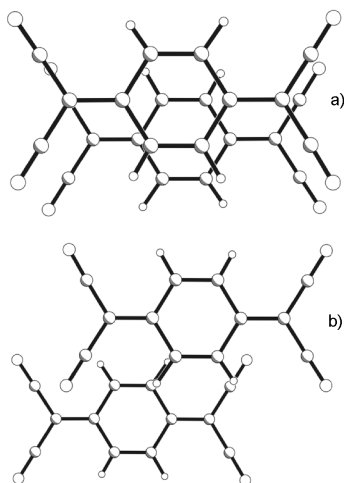


Fig. 2. Overlapping of TCNQ anion-radicals in (I): within pairs (a); between pairs (b)

layered structure (Fig. 1), where cation layers alternate along the c axis with those consisting of TCNQ anion-radicals. Anionic layers differ from each other by the molecular symmetry therein: the BC layers formed by center-symmetrical B and C anions, alternate with A ones, consisting of A anions without any crystallographic symmetry elements. In A and BC layers, the anions overlap in various manners: in A layers, neighboring anions are shifted with respect to each other along the long axis at a C=C distance; in BC layers, anions practically are not overlapped (Fig. 3). Fig. 1 also shows the stacks of A and B-C anions. Interplanar A...A distances are 3.21 Å, C...B...C distances are 3.45 Å. The dihedral angles between the planes drawn through all carbon atoms are 0.0° and 9.8° for A...A and C...B...C molecules, respectively. Cations and anions in (II) are practically planar, maximum atomic deviation out of the cation plane is 0.08 Å (C(2) atom). Maximum atomic deviations out of anion planes are 0.05 Å (N(4) atom), 0.03 Å (C(24) atom), and 0.08 Å (C(31) atom) for A, B, and C anion-radicals, respectively. Charges of A, B and C particles, calculated are: $A^{-0.60}$, $B^{0.28}$, $C^{-0.88}$.

The broadened lines in the spectra (I) (with maxima at 1128, 1325, 2158 cm^{-1}) and (II) (with maxima at 1094, 1279, 2147 cm^{-1}) presented in Fig. 4 are observed against the background of the continuous absorption caused by excitation of conductivity electrons. The onset of this absorption corresponds to the band gap width. Back to the onset of the continuous absorption ν_{min} , we have estimated the conductivity activation energy Δ for both this

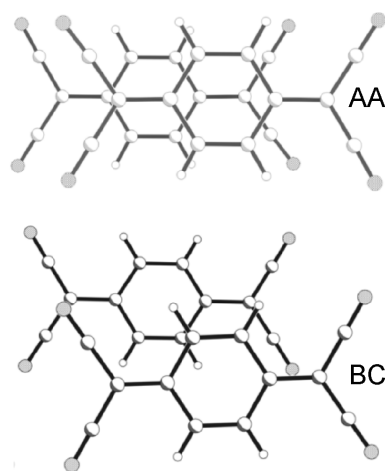


Fig. 3. Overlapping of TCNQ anion-radicals in (II).

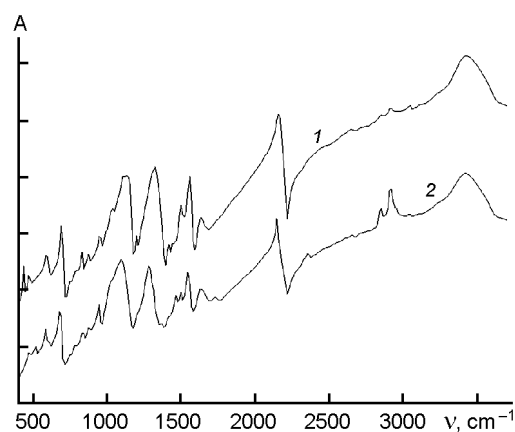


Fig. 4. IR-spectra of (I) and (II).

ARS: $\nu_{min} \approx 750 \text{ cm}^{-1}$ which yields $\Delta \approx 0.09 \text{ eV}$. This suggests the similarity of electric conducting properties of ARS (I) and (II). However, electric conductivities of these ARS at room temperature differ almost by three decimal orders: $\sigma_{RT}(\text{I}) = 3.9 \cdot 10^{-5} \Omega^{-1} \text{cm}^{-1}$, and $\sigma_{RT}(\text{II}) = 2.4 \cdot 10^{-2} \Omega^{-1} \text{cm}^{-1}$. The temperature dependence of electric resistance for both ARS can be described by a simple activation model, but with essentially different parameters, namely, for (I): $\ln(R/RRT) = -8.81 + 2522.1/T$ (correlation coefficient 99.91 %); for (II): $\ln(R/RRT) = -5.045 + 1476.4/T$ (correlation coefficient 99.82 %). That difference is probably connected with the dimerization of TCNQ stacks in (I), whereas the higher electric conductivity of (II) can be associated with homogeneous layers consisting of A particles. Such influence of

small structural differences is observed for all ARS TCNQ with pyrazinium-based cations synthesized by us [4–6]: positions of substituents in pyrazine as well as length of alkyl-radical in cations give rise to small structural changes (mainly distances in TCNQ stacks) but sufficient changes in physical properties.

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Нові аніон-радикальні солі (N–Me–2,5–di–MePz)(TCNQ)₂ та (N–Me–2,6–di–MePz)(TCNQ)₂ (Pz — піразин)

*О.М.Кажева, Д.В.Зіолковський, Г.Г.Александров,
О.А.Дьяченко, В.О.Стародуб, А.В.Хоткевич, Г.Ю.Василець*

Вперше синтезовано аніон-радикальні солі 7,7,8,8-тетраціанохінодіметану (TCNQ) з катіонами N-метил-2,5-діметилпіразинію (N–Me–2,5–di–Me–Pz)⁺ та N-метил-2,6-діметилпіразинію (N–Me–2,6–di–Me–Pz)⁺. Проведено PCA монокристалів, визначено молекулярну та кристалічну будову, досліджено ІЧ-спектри та електропровідність в широкому діапазоні температур.