

A novel anion-radical salt (N-Et-2.5-di-Me-Pz)(TCNQ)₂ (Pz is pyrazine)

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Synthesis, structure and properties of the new tetracyanoquinodimethane anion-radical salt (ARS) having the composition (N-Et-2.5-di-Me-Pz)(TCNQ)₂ (Pz is pyrazine) are reported. The compound has a layered structure where conducting anion-radical layers formed by TCNQ alternate with non-conducting cation layers along the *a* axis. The charges of TCNQ particles in the stack alternate, i.e. are localized appreciably, which can account for a rather unusual temperature dependence of electric resistance. Such a peculiarity of structure renders to the ARS electronic system a somewhat two-dimensional character that is unusual for TCNQ ARS and agrees with the electrophysical measurements.

Описаны синтез и свойства новой анион-радикальной соли (АРС) тетрацианохиноди-метана состава (N-Et-2,5-di-Me-Pz)(TCNQ)₂ (Pz — пиразин). Соединение имеет слоистую структуру, в которой проводящие анион-радикальные слои, образованные TCNQ, чередуются с непроводящими катионными слоями вдоль оси *a*. Заряды частиц TCNQ в стопках альтернируют, то есть, заметно локализованы, что может быть причиной необычной температурной зависимости электросопротивления. Такая особенность структуры придает электронной системе АРС определенную двумерность, необычную для АРС TCNQ, и согласуется с результатами электрофизических измерений.

Anion-radical salts (ARS) of TCNQ have been recently in the focus of attention due to their wide range of possible applications [1–3] and due to the discovery of ARS capable of forming magnetically ordered structures [4–6]. ARS of NMP–TCNQ (NMP is N-methylphenazinium ion) was one of the first organic metals where, however, transition to the Mott dielectric state was observed at $T_M \approx 220$ K [7]. However, after the discovery of organic metals and subsequently of superconductors based on cation radical salts (CRS) of tetrathiafulvalene and its derivatives [8], the interest to TCNQ

ARS was weakened considerably. In spite of a long history of TCNQ chemistry, no ARS with pyrazine (Pz) derivatives as a cation are known. Pyrazine is the simplest analogue of phenazine being a constituent of the first organic metal, NMP–TCNQ.

TCNQ ARS with N-alkylpyrazinium cations are of a particular interest. Including a nonalkylated nitrogen atom, such a cation may interact quite specifically with anion-radicals or, due to donor-acceptor interaction, with metal cations, which may result in formation of supramolecular structures. Recently [9], we have synthesized the first

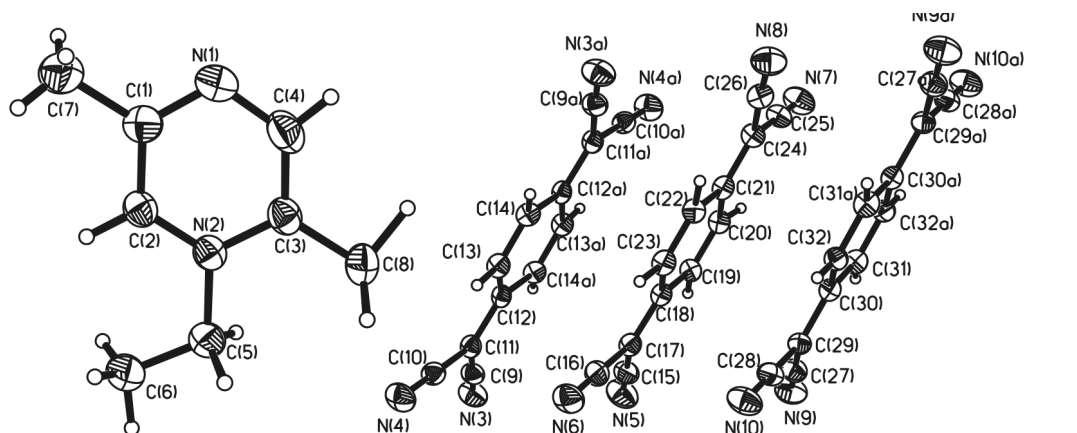
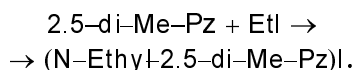


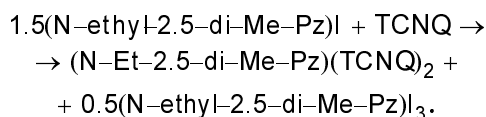
Fig. 1. Cation [N-Et-2.5-di-Me-Pz]⁺ and anion-radicals TCNQ in [N-Et-2.5-di-Me-Pz](TCNQ)₂. Atoms are shown as 50 % thermal probability ellipsoids.

ARS of TCNQ, (N-Et-Pz)(TCNQ)₃, having a quasi-two-dimensional structure (all the previously known ARS of TCNQ are one-dimensional). The quasi-two-dimensional character of this ARS follows from its structure and the analysis of its electro-physical and optical properties. In this paper, we report the synthesis, crystal and molecular structures, IR spectra and electro-physical properties of a new TCNQ ARS, (N-Et-2.5-di-Me-Pz)(TCNQ)₂.

Synthesis. 2.5-Di-Me-Pz obtained from Aldrich was used in the experiment. TCNQ was purified by vacuum zone sublimation. Ethyl iodide was synthesized using reaction of ethanol with phosphorus triiodide followed by distillation in an inert medium. N-Ethyl-2.5-di-Me-Pz iodide was prepared using the reaction:



(N-Et-2.5-di-Me-Pz)(TCNQ)₂ ARS was obtained as follows:



The ARS precipitate was filtered, washed with ether-acetone mixture and ether and dried in vacuum. In order to grow single crystals and for purification, recrystallization from acetone was used. Black-violet parallelepiped-shaped crystals up to 2 mm length have been obtained. The ARS composition was determined spectrophotometrically in acetonitrile as described in [9] and confirmed by X-ray analysis.

X-ray Diffraction. The X-ray diffraction examination on (N-Et-2.5-di-Me-Pz)(TCNQ)₂

crystals was carried out using a KM-4 KUMA DIFFRACTION diffractometer ($\omega/2\theta$ -scanning, Mo-K α radiation, graphite monochromator). The crystal structure was solved by direct methods and following Fourier synthesis using the SHELXS-97 software package [10]. The structure was refined by full-matrix least squares procedures using an anisotropic approximation for all non-hydrogen atoms with the SHELXS-97 program [11]. An absorption correction was applied using the DIFABS program.

The crystal structure of (N-Et-2.5-di-Me-Pz)(TCNQ)₂ is formed by TCNQ anion-radicals and (N-Et-2.5-di-Me-Pz)⁺ cations (Fig. 1). Three types of TCNQ anion-radicals (A, B and C) of different local symmetries have been revealed in the crystal unit cell. The anion-radicals A and C are in special center-symmetrical positions while the anion-radical B is in the general one. Main crystallographic parameters and details of the experiment are presented in Table 1.

The ORTEP drawings as well as full tables of fractional atomic coordinates and interatomic bond distances are deposited at the Cambridge Crystallographic Data Center (deposition No.CCDC 258349). The bond lengths and valence angles are listed in Tables 2 and 3, enumeration of atoms is shown in Fig. 1; Fig. 2 shows the structure projection along the *a* axis.

The synthesized compound was studied by two experimental techniques: absorption measurements in the infrared (IR) spectral range and the electric conductivity studies of the obtained samples. When measuring the IR absorption spectra, the pelleting in KBr was applied, with registration at room temperatures on a Specord-75 IR spectrophotometer, wave numbers ranging from

Table 1. Crystal data for [N-Et-2.5-di-Me-Pz](TCNQ)₂

Chemical formula	C ₃₂ H ₂₁ N ₁₀
Chemical formula mass	545.59
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Temperature, K	295
<i>a</i> , Å	25.291(5)
<i>b</i> , Å	15.505(3)
<i>c</i> , Å	7.121(1)
β, °	94.71(3)
<i>V</i> (Å ³)	2783.0(1)
<i>Z</i>	4
<i>D</i> _{calc.} (g·cm ⁻³)	1.30
Radiation type	Mo K _α
μ, mm ⁻¹	0.083
Diffractometer	KM-4 KUMA DIFFRACTION
Data collection method	1/2θ
Total number of reflections	6205
Number of unique reflections	5408
Number of observed reflections	1815
[<i>F</i> ₀ > 4σ(<i>F</i> ₀)]	
Number of refined parameters	380
(2θ) _{max} , °	52.14
Range of <i>h</i> , <i>k</i> , <i>l</i>	-31 → <i>h</i> → 31 0 → <i>k</i> → 19 0 → <i>l</i> → 8

Table 2. Bond lengths (Å) in [N-Et-2.5-di-Me-Pz](TCNQ)₂

N(1)–C(1)	1.321(3)	C(12)–C(13)	1.416(3)
N(1)–C(4)	1.331(4)	C(12)–C(14)#1	1.418(3)
N(2)–C(2)	1.329(3)	C(13)–C(14)	1.355(3)
N(2)–C(3)	1.344(3)	C(15)–C(17)	1.418(3)
N(2)–C(5)	1.492(3)	C(16)–C(17)	1.433(3)
N(3)–C(9)	1.140(3)	C(17)–C(18)	1.370(3)
N(4)–C(10)	1.141(3)	C(18)–C(19)	1.430(3)
N(5)–C(15)	1.141(3)	C(18)–C(23)	1.434(3)
N(6)–C(16)	1.126(3)	C(19)–C(20)	1.340(3)
N(7)–C(25)	1.134(3)	C(20)–C(21)	1.443(3)
N(8)–C(26)	1.136(3)	C(21)–C(24)	1.378(3)
N(9)–C(27)	1.144(3)	C(21)–C(22)	1.439(3)
N(10)–C(28)	1.140(3)	C(22)–C(23)	1.335(3)
C(1)–C(2)	1.371(3)	C(24)–C(26)	1.421(3)
C(1)–C(7)	1.486(4)	C(24)–C(25)	1.422(3)
C(3)–C(4)	1.366(4)	C(27)–C(29)	1.414(3)
C(3)–C(8)	1.501(4)	C(28)–C(29)	1.412(3)
C(5)–C(6)	1.468(4)	C(29)–C(30)	1.399(3)
C(9)–C(11)	1.419(3)	C(30)–C(31)	1.417(3)
C(10)–C(11)	1.420(3)	C(30)–C(32)	1.419(3)
C(11)–C(12)	1.400(3)	C(31)–C(32)#2	1.349(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y + 1, -z + 2$; #2 $-x, -y, -z + 2$

400 to 3000 cm⁻¹. The spectrum is shown in Fig. 3. The DC electric conductivity of single crystals of the synthesized salt was measured in temperature range of 160 to 300 K using the four contact scheme.

The compound has a layered structure where conducting anion-radical layers formed by TCNQ alternate with non-conducting cation layers along the *a* axis (Fig. 2). The TCNQ anion-radicals are packed in stacks along the *b* axis in A...B...C...B... sequence (Fig. 4). Bond lengths and valence angles are presented in Table 2. Considering the bond lengths we estimated the quinoidity degree and the charges of the particles A, B, C using the same calculation procedure as in [9]. The calculation results are presented in Table 4. According to these data, the charge in TCNQ stacks is distributed unhomogeneously: the particles A and C have the charge of approximately $-2/3$ while the B one is charged three times lower. Thus, the charges of TCNQ particles

in the stack alternate, i. e. are localized appreciably, which may account for a rather unusual temperature dependence of electric resistance (see below). TCNQ anion-radicals are characterized by a relatively equal degree of deviation from the planar conformation: maximal deviation of the atoms from the average anion-radical plane is ± 0.03 Å for N(3) and N(3a) atoms of A anion, 0.06 Å for the N(5) atom of anion B and ± 0.02 Å for C(31) and C(31a) atoms of anion C. The interplane distance between TCNQ anions in stacks ranges from 3.24 to 3.33 Å: A...B 3.25 Å, B...C 3.27 Å, C...B 3.33 Å, B...A 3.24 Å. Dihedral angles between the planes of TCNQ anion-radicals are $0.7 \div 2.2^\circ$: A...B 0.7° , B...C 2.2° , C...B 2.1° , B...A 0.7° . Shortened hydrogen contacts of C–H...N type have been revealed between cations and anions. The anion A is connected with two cations by hydrogen bonds C(8)–H(13)...N(3): C(8)–H(13) 1.17 Å, H(13)...N(3) 2.42 Å, the angle C(8)–H(13)...N(3) 144.0 . A slightly

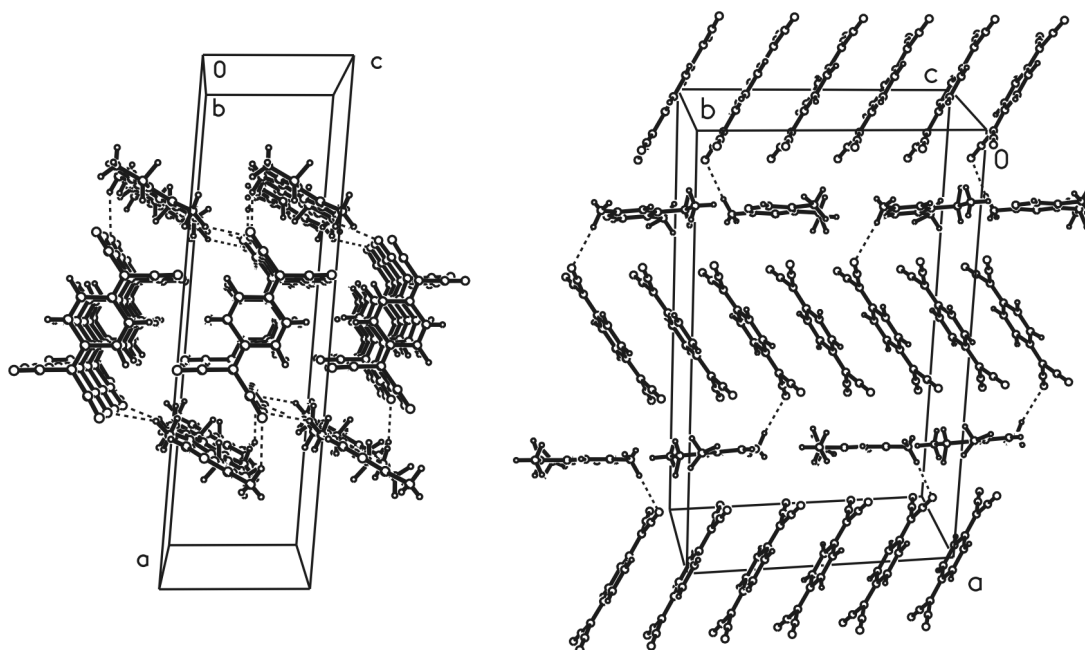


Fig. 2. Crystal structure of $[N\text{-Et-2.5-di-Me-Pz}](\text{TCNQ})_2$. Alternation of conducting and non-conducting layers along the a axis. Dotted line marks short intermolecular contacts.

shortened intermolecular contacts were found between the cation and anion layers: $[C(2)\text{-}H(1)\dots N(9): C(2)\text{-}H(1) 0.98 \text{ \AA}, H(1)\dots N(9) 2.57 \text{ \AA},$ the angle $C(2)\text{-}H(1)\dots N(9) 157.1^\circ]$, which may be responsible for charge transfer not only along the TCNQ stacks but in perpendicular direction as well.

The cation layer $[N\text{-Et-2.5-di-Me-Pz}](\text{TCNQ})_2$ is formed by rows of cations along the b axis (Fig. 2). The cations are practically planar, their maximal deviation from the plane is 0.02 \AA for $C(1)$ atom. The dihedral angles between the planes of cation and anion-radicals are $125.2, 124.6, 123.6^\circ$ for A, B, C molecules, respectively. The $N\text{-C}$ distance in the cation cycle $[N\text{-Et-2.5-di-Me-Pz}]^+$ ranges from $1.321(3)$ to $1.344(3) \text{ \AA}$, the $C\text{-C}$ distances are $1.366(4)$ and $1.371(3) \text{ \AA}$, and the angles in the cycle range from $115.5(2)$ to $125.8(3)^\circ$. The distances in ethyl substituent are as follows: $N(2)\text{-}C(5), 1.492(3) \text{ \AA}, C(5)\text{-}C(6), 1.468(4) \text{ \AA},$

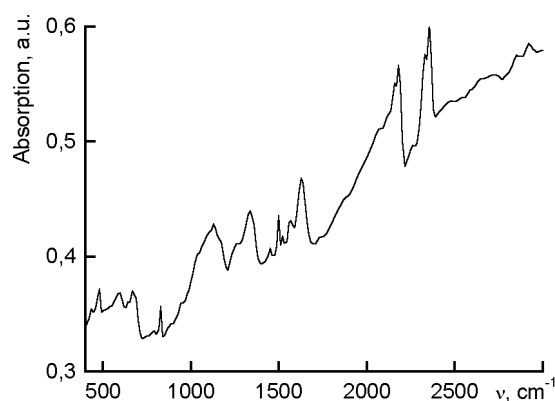


Fig. 3. IR-spectrum of $[N\text{-Et-2.5-di-Me-Pz}](\text{TCNQ})_2$.

the angle $C(6)\text{-}C(5)\text{-}N(2), 114.9(2)^\circ,$ $C(2)\text{-}N(2)\text{-}C(5), 121.9(2)^\circ,$ $C(3)\text{-}N(2)\text{-}C(5), 118.6(2)^\circ$. The distances with methyl substituents are: $C(1)\text{-}C(7), 1.486(4) \text{ \AA}$ and $C(3)\text{-}C(8), 1.501(4) \text{ \AA}$.

Table 4. *HOSE* model data (kJ/mol) for a three TCNQ species in $(N\text{-Et-2.5-di-Me-Pz})(\text{TCNQ})_2$ ARS and Flandrois&Chasseau charge Q

Species	$HOSE_i$	Quinoidity, %	$HOSE_i$	Kekule's structure, %	$HOSE_{tot}$	Q
A	22.74	59.5	66.83	40.5	40.60	-0.69
B	8.53	83.3	85.03	16.7	21.32	-0.17
C	21.56	62.3	71.22	37.7	40.29	-0.63

Table 3. Valence angles (°) in [N-Et-2.5-di-Me-Pz](TCNQ)₂

C(1)–N(1)–C(4)	115.5(2)	C(15)–C(17)–C(16)	114.2(2)
C(2)–N(2)–C(3)	119.5(2)	C(17)–C(18)–C(19)	120.9(2)
C(2)–N(2)–C(5)	121.9(2)	C(17)–C(18)–C(23)	121.8(2)
C(3)–N(2)–C(5)	118.6(2)	C(19)–C(18)–C(23)	117.3(2)
N(1)–C(1)–C(2)	121.5(3)	C(20)–C(19)–C(18)	121.2(2)
N(1)–C(1)–C(7)	118.6(3)	C(19)–C(20)–C(21)	121.5(2)
C(2)–C(1)–C(7)	119.8(3)	C(24)–C(21)–C(22)	121.2(2)
N(2)–C(2)–C(1)	121.2(2)	C(24)–C(21)–C(20)	121.9(2)
N(2)–C(3)–C(4)	116.6(3)	C(22)–C(21)–C(20)	116.9(2)
N(2)–C(3)–C(8)	120.4(2)	C(23)–C(22)–C(21)	121.1(2)
C(4)–C(3)–C(8)	123.0(2)	C(22)–C(23)–C(18)	121.9(2)
N(1)–C(4)–C(3)	125.8(3)	C(21)–C(24)–C(26)	124.0(2)
C(6)–C(5)–N(2)	114.9(2)	C(21)–C(24)–C(25)	121.2(2)
N(3)–C(9)–C(11)	178.2(3)	C(26)–C(24)–C(25)	114.8(2)
N(4)–C(10)–C(11)	178.0(3)	N(7)–C(25)–C(24)	178.9(3)
C(12)–C(11)–C(9)	122.9(2)	N(8)–C(26)–C(24)	176.4(3)
C(12)–C(11)–C(10)	122.2(2)	N(9)–C(27)–C(29)	180.0(4)
C(9)–C(11)–C(10)	114.9(2)	N(10)–C(28)–C(29)	178.6(3)
C(11)–C(12)–C(13)	121.3(2)	C(30)–C(29)–C(28)	121.9(2)
C(11)–C(12)–C(14)#1	121.7(2)	C(30)–C(29)–C(27)	122.5(2)
C(13)–C(12)–C(14)#1	117.0(2)	C(28)–C(29)–C(27)	115.6(2)
C(14)–C(13)–C(12)	122.0(2)	C(29)–C(30)–C(31)	122.3(2)
C(13)–C(14)–C(12)#1	121.0(2)	C(29)–C(30)–C(32)	121.8(2)
N(5)–C(15)–C(17)	178.2(3)	C(31)–C(30)–C(32)	116.0(2)
N(6)–C(16)–C(17)	177.7(3)	C(32)#2–C(31)–C(30)	121.7(2)
C(18)–C(17)–C(15)	123.6(2)	C(31)#2–C(32)–C(30)	122.36(19)
C(18)–C(17)–C(16)	122.2(2)		

The broadened lines in the spectra (with maxima at 1130, 1335, 2180 cm⁻¹) presented in Fig. 3 are observed on the background of the continuous absorption caused by the excitation of conductivity electrons. The beginning of this absorption corresponds to the band gap width. Basing on the beginning of continuous absorption ν_{min} , we have estimated the conductivity activation energy Δ for this ARS: $\nu_{min} \approx 850$ cm⁻¹ which yields $\Delta \approx 0.105$ eV. However, a simple activation model does not allow us to describe adequately the temperature dependence of electric resistance of ARS [N-Et-2.5-di-Me-Pz](TCNQ)₂, so we have invoked the model based on the hopping mechanism of conductivity, possibly conditioned by the structural peculiarities of the this ARS [12]:

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

Here, α is the system dimensionality; T_0 and A , the model parameters. For the (N-Et-2.5-di-Me-Pz)(TCNQ)₂ compound, the best fit of the experimental and theoretical $R(T)$ dependences is observed for $\alpha = 2$ (Fig. 5), which corresponds to two-dimensional case. The logarithm of the reduced electric resistance R/R_{RT} is expressed as

$$\ln(R/R_{RT}) = -14.18 + \frac{93.43}{T^{1/3}}.$$

Thus, results of resistance measurements confirm essentially quasi-two-dimensional conductivity character of this ARS due to the features of its crystal structure.

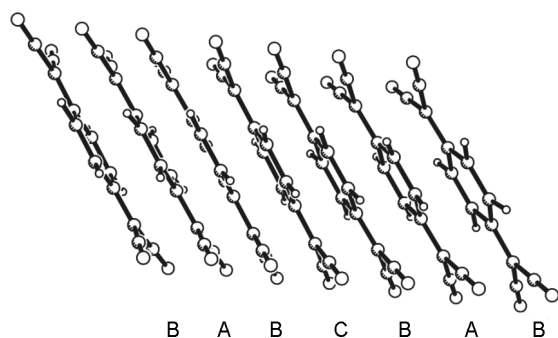


Fig. 4. A stack of TCNQ anion-radicals in $[N\text{-Et-2.5-di-Me-Pz}](\text{TCNQ})_2$.

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References

1. Sanyo Electric Co. Ltd., Saga Sanyo Industries Co Ltd., United States Patent No.5,766,271 (1998).
2. Nippon Chem-Con Corporation, United States Patent No.6,504,704 (2003).
3. Advanced Micro Devices, Inc., United States Patent No.6,809,955 (2004).
4. T.Sugimoto, K.Ueda, M.Tsujii et al., *Chem. Phys. Lett.*, **249**, 304 (1996).
5. K.Ueda, T.Sugimoto, S.Endo et al., *Chem. Phys. Lett.*, **261**, 295 (1996).
6. K.Mukaji, S.Jinno, Y.Shimobe et al., *Polyhedron*, **20**, 1537 (2001).
7. I.F.Schegolev, *Phys. Stat. Sol. Ser. a*, **12**, 9 (1972).
8. D.Jerome, A.Masaud, M.Ribault et al., *J. Phys. Lett.*, **290**, B27 (1980).
9. D.V.Ziolkovskiy, A.V.Kravchenko, V.A.Starodub et al., *Functional Materials* **12**, 3 (2005).
10. G.M.Sheldrick, SHELXS-97, Program for Crystal Structure Determination, University of Goettingen, Germany (1997).
11. G.M.Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Goettingen, Germany (1997).
12. J.M.Ziman, *Models of Disorder*, Cambridge University Press, Cambridge, London, New York, Melbourne (1979).

Нова аніон-радикальна сіль (N-Et-2,5-ді-Ме-Рз)(ТСNQ)₂ (Рз — піразин)

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Описано синтез та властивості нової аніон-радикальної солі (АРС) тетраціанохінодіметану складу $(N\text{-Et-2,5-ді-Ме-Рз})(\text{TCNQ})_2$ (Рз — піразин). Сполука має шарувату структуру, в якій провідні аніон-радикальні шари, утворені ТСNQ, чередуються з непровідними катіонними шарами уздовж осі *a*. Заряди часток ТСNQ в стопках альтернують, тобто, суттєво локалізовані, що може бути причиною незвичайної температурної залежності електроопору. Така особливість структури додає електронній системі АРС певну двомірність, незвичайну для АРС ТСNQ, і добре узгоджується з результатами електрофізичних вимірів.

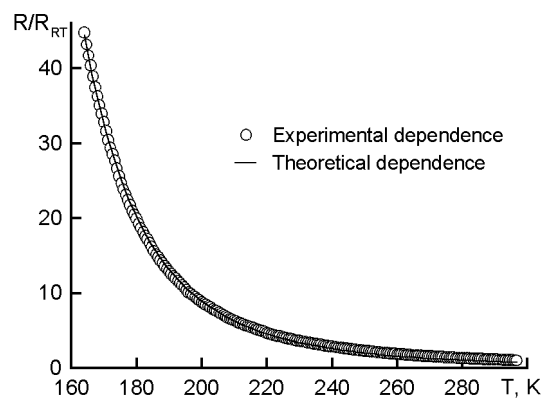


Fig. 5. Temperature resistance dependences for ARS $[N\text{-Et-2.5-di-Me-Pz}](\text{TCNQ})_2$.