Functional Materials 12, No.3 (2005)

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

D.V.Ziolkovskiy, A.V.Kravchenko, V.A.Starodub, O.N.Kazheva[*], *A.V.Khotkevich*[**]

V.Karazin Kharkiv National University,
4 Svobody Sq. 61077 Kharkiv, Ukraine
[*]Institute for Problems of Chemical Physics, Russian Academy of Sciences, 1 Semenov Ave., 142432 Chernogolovka, Moscow Region
[**]B.Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine,
47 Lenin Ave., 61108 Kharkiv, Ukraine

Received July 28, 2004

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_5C_2)–Pz](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 bulks 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-тетрацианохинодиметана (TCNQ) необычного состава [N–(H_5C_2)–Pz](TCNQ)$_3$, где Pz — пиразин. Структура данной АРС также необычна — в отличие от большинства известных структур, она состоит из стопок, образованных двумя типами TCNQ — *A* и *C*, перпендикулярно которым расположены частицы третьего типа — *B*. Частицы типа *C* заметно взаимодействуют с катионами пиразина посредством неалкилированного атома азота пиразина. Частицы типа *B*, как и частицы TCNQ в стопках, обладают заметным зарядом (около –0,3). Такая особенность структуры придает электронной системе АРС определенную двумерность, необычную для АРС TCNQ, и согласуется с результатами электрофизических измерений.

TCNQ based ARS gave impetus to the researches late in sixties in view of the problem of hightemperature 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 tetrathiafulvalene and its derivatives [3] 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 operational characteristics, namely, the ability to "self-treatment" of oxide layer defects [8]. Electrophysical and optical researchs 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 cations 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 interaction 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_3C)–Pz](TCNQ) composition is also an organic metal, in which a metallic state is stable down to 120 K. This seems to be an extremely low metal-dielectric transition temperature for ARS of TCNQ with cations of a "closed" type.

Synthesis, crystalline and molecular structure, optical and electrophysical properties of the novel ARS of unusual composition [N–(H_5C_2)–Pz](TCNQ)$_3$ (NEPz–(TCNQ)$_3$) are described in this article. This ARS is the first example of TCNQ salt with quasi-two-dimensional electonic 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; ethyliodide 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:

$$Pz + EtI \rightarrow (NEPz)I.$$

NEPz–(TCNQ)$_3$ ARS was obtained by:

$$1.5(NEPz)I + 3TCNQ \rightarrow$$
$$\rightarrow NEPz - (TCNQ)_3 + 0.5(NEPz)(I_3).$$

ARS precipitate was filtered, washed with ether and hexane and dried under vacuum. In order to grow single crystals and for purification recrystallization from acetone was used. Black-violet needle crystals with length up to 3 mm had been obtained. ARS composition was determined spectrophotometrically in acetonitrile by measuring optical density both at 394 nm, where anion-radicals as well as TCNQ molecule absorb, and at 840 nm, where anion-radicals only absorb. Composition of salt in acetonitryle solution may be determined by the relation:

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

where D_λ — optical density on the respective wavelength.

$C_{42}H_{21}N_{14}$, M = 721.72 g/mol; monoclinic, space group $C2/m$, $Z = 4$, $a = 3699.8(7)$, $b = 1264.0(3)$, $c = 656.80(33)$ pm, $\alpha = 90$, $\beta = 91.24(3)$, $\gamma = 90$ deg, $V = 3070.8(11)\cdot10^6$ pm^3, Mo–K_α, $T = 293(2)$ K. A difractometer STOE STADI4 with flat detector had been used for data collecting. 3028 independent reflections ($R_{int} = 0.1267$) were chosen from 9808 ones. The structure was determined by direct (SHELXS-97) method and refined by full-matrix method of least-squares for F^2 in anisotropic approximation [12]. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced geometrically and refined according a "rider" model with $U_{iso} = 1.2U_{equiv}$ of the respective carbon atom. Largest diffusion peak and hole: 0.246 and –0.227 e/Å^3. 275 parameters, all heavy atoms being anisotropic. Final validity data are: *R1* and *wR2* values were 0.0767 [$I > 2\sigma(I)$] and 0.1877 respectively along the whole range of independent reflections; $S = 1.00$. The weighting function used was $w = 4F_0^2/\sigma^2(F_0^2)$ for the function of $\sum_w(|F_0|-|F_C|)^2$ to be minimized. The ORTEP drawings, and full tables of fractional atomic coordinates and interatomic bond distances, have been deposited 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–$(TCNQ)_3$

C(1)–N(1)	114.1(5)	C(13)–N(4)	115.1(5)
C(1)–C(2)	141.6(5)	C(13)–C(14)	141.0(5)
C(2)–C(3)	138.3(7)	C(14)–C(15)	140.9(7)
C(2)–C(1)#1	141.6(5)	C(14)–C(13)#1	141.0(5)
C(3)–C(4)#1	144.0(4)	C(15)–C(16)	143.1(4)
C(3)–C(4)	144.0(4)	C(15)–C(16)#1	143.1(4)
C(4)–C(5)	134.5(5)	C(16)–C(17)	136.0(5)
C(5)–C(6)	143.3(4)	C(17)–C(18)	142.4(4)
C(6)–C(7)	138.9(7)	C(18)–C(19)	141.1(7)
C(6)–C(5)#1	143.3(4)	C(18)–C(17)#1	142.4(4)
C(7)–C(8)#1	143.0(5)	C(19)–C(20)#1	140.8(5)
C(7)–C(8)	143.0(5)	C(19)–C(20)	140.8(5)
C(8)–N(2)	114.8(5)	C(20)–N(5)	114.7(5)
C(9)–N(3)	112.9(6)	C(21)–N(6)	131.4(5)
C(9)–C(10)	143.7(6)	C(21)–C(22)	137.1(7)
C(10)–C(11)	137.6(8)	C(22)–N(7)	135.0(5)
C(10)–C(9)#2	143.7(6)	C(23)–C(24)	148.5(14)
C(11)–C(12)	143.1(5)	C(23)–N(7)	150.3(8)
C(11)–C(12)#2	143.1(5)	N(6)–C(21)#1	131.4(5)
C(12)–C(12)#1	134.7(9)	N(7)–C(22)#1	135.0(5)

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

N(1)–C(1)–C(2)	177.5(5)	N(4)–C(13)–C(14)	177.8(5)
C(3)–C(2)–C(1)	122.6(2)	C(15)–C(14)–C(13)#1	120.7(2)
C(3)–C(2)–C(1)#1	122.6(2)	C(15)–C(14)–C(13)	120.7(2)
C(3)–C(2)–C(1)#1	114.8(5)	C(13)#1–C(14)–C(13)	118,6(5)
C(2)–C(3)–C(4)#1	121.4(2)	C(14)–C(15)–C(16)	121.3(2)
C(2)–C(3)–C(4)	121.4(2)	C(14)–C(15)–C(16)#1	121.3(2)
C(4)–C(3)–C(4)	117.2(5)	C(16)–C(15)–C(16)#1	117.5(5)
C(5)–C(4)–C(3)	121.6(4)	C(17)–C(16)–C(15)	121.0(4)
C(4)–C(5)–C(6)	120.2(4)	C(16)–C(17)–C(18)	121.4(4)
C(7)–C(6)–C(5)	120.5(2)	C(19)–C(18)–C(17)#1	121.2(2)
C(7)–C(6)–C(5)#1	120.5(2)	C(19)–C(18)–C(17)	121.2(2)
C(5)–C(6)–C(5)#1	119.0(5)	C(17)#1–C(18)–C(17)	117.6(5)
C(6)–C(7)–C(8)#1	122.9(2)	C(20)#1–C(19)–C(18)	116.2(5)
C(6)–C(7)–C(8)	122.9(2)	C(20)#1–C(19)–C(18)	121.9(2)
C(8)#1–C(7)–C(8)	114.2(5)	C(20)–C(19)–C(18)	121.9(2)
N(2)–C(8)–C(7)	178.0(5)	N(5)–C(20)–C(19)	179.5(5)
N(3)–C(9)–C(10)	174.8(6)	N(6)–C(21)–C(22)	123.6(5)
C(1)–C(10)–C(9)#2	123.3(3)	N(7)–C(22)–C(21)	118.4(5)
C(11)–C(10)–C(9)	123.3(3)	C(24)–C(23)–N(7)	109.4(7)
C(9)#2–C(10)–C(9)	113.3(6)	C(21)–N(6)–C(21)	116.7(6)
C(10)–C(11)–C(12)	120.7(3)	C(22)#1–N(7)–C(22)	119.4(6)
C(10)–C(11)–C(12)#2	120.7(3)	C(22)#1–N(7)–C(23)	120.3(3)
C(12)–C(11)–C(12)#2	118.7(6)	C(22)–N(7)–C(23)	120.3(3)
C(12)#1–C(12)–C(11)	120.7(3)		

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

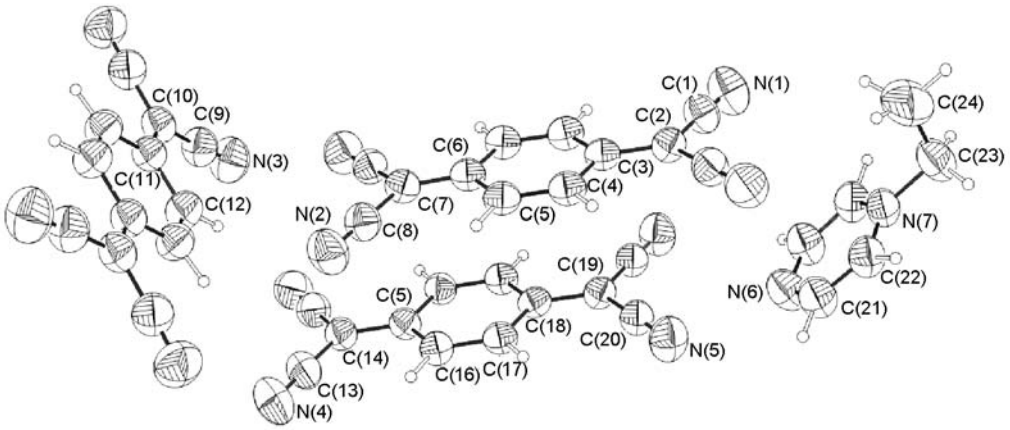

Fig. 1. ORTEP view and atom labeling of NEPz–$(TCNQ)_3$.

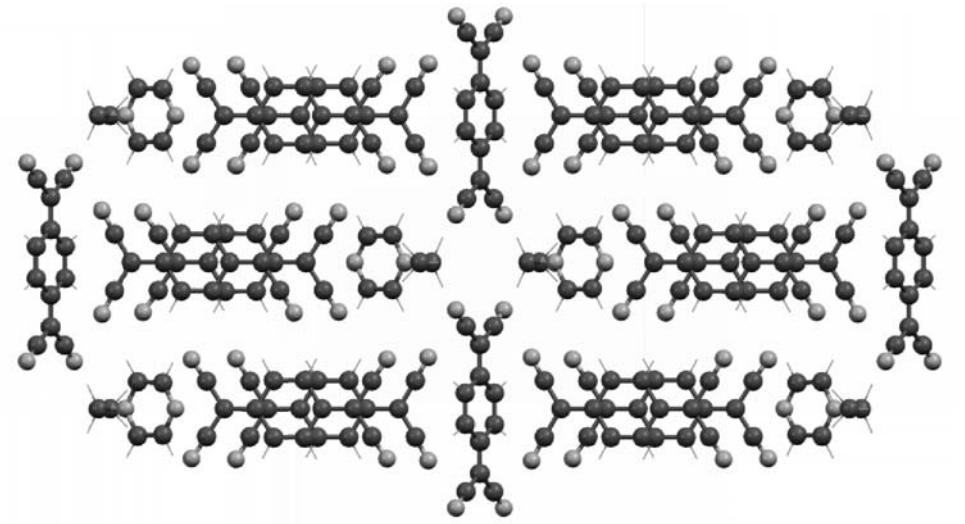

Fig. 2. The structure projection along plane [010].

tric conductivity of the obtained samples. In the studies of IR absorption spectra a technique of pelletting 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 TCNQ 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 TCNQ particles) in order to interpret the results of electrophysical measurements. As the degree of quinoidity decreases when electron is added to the TCNQ molecule, the latter is in a definite dependence upon TCNQ charge. The degree of quinoidity may be determined with bond lengths in TCNQ 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 TCNQ charge with correlation coefficient of $r = 0.992$. Proceeding from the data in Table 1, we calculated HOSE energies for quinoid and Kekule's TCNQ structures for *A*, *B* and *C* particles and their charges (see Table 3).

Table 3. HOSE model data (kJ/mol) for a three TCNQ species in NEPz–$(TCNQ)_3$ ARS and Flandrois&Chasseau charge Q

Species	$HOSE_i$	% Quinoidity	$HOSE_i$	% Kekule's structure	$HOSE_{tot}$	Q
A	6.17	86.6	79.71	13.5	16.03	0.10
B	11.19	77.1	75.18	22.9	25.88	0.31
C	17.00	65.4	64.40	34.5	33.39	0.56

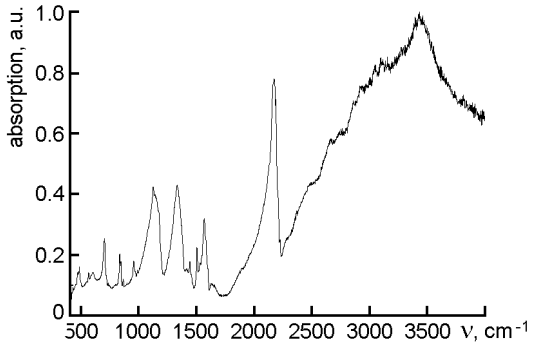

Fig. 3. IR-spectra of NEPz–$(TCNQ)_3$.

According to the data obtained the charge in a columns is distributed quite irregularly — C type particles (that interact with pyrazinium cation) possess much larger charge −0.55 e than A particles −0.10 e. At the same time B particles also possess quite a large charge −0.31 e. Due to such peculiarity of ARS NEPz–$(TCNQ)_3$ crystalline and electronic structure the latter has unusual for TCNQ salts quasi-two-dimensional conducting character because electrons can move not only along the columns, but also in the direction perpendicular to them. As Fig. 2 shows, TCNQ columns are divided by cations in ARS structure, but linked with nearly perpendicular located TCNQ particles of B-type with −0.31 e charge.

Broadened lines in the spectra presented in Fig. 3 are observed on the background of the continuous absorption caused by the excitation of conductivity electrons. Beginning of this absorption corresponds to the width of the forbidden band. Back to the beginning of continuous absorption ν_{min} we have estimated energy of conductivity activation Δ for this ARS: $\nu_{min} \approx 1750$ cm^{-1} which yields $\Delta \approx 0.22$ eV.

For adequate description of the temperature behavior of electric resistance of ARS NEPz–$(TCNQ)_3$ we have invoked the model based on the hopping mechanism of conductivity possibly conditioned by the structural peculiarities of the this ARS [15]:

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

Here α 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:

$$\ln (R/R_{RT}) = -21.85 + \frac{175.20}{T^{1/3}}.$$

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.

This research was carried on at financial support of the STCU (grant No.2276) and RFBR (grant No.02-03-32794). The authors thank Prof.D.Fenske and Dr.A.Rothenberger from the University (TH) Karlsruhe for their cooperation and fruitful discussions.

References

1. W.A.Little, *Phys. Rev. A.*, **134**, 1416 (1964).
2. I.F.Schegolev, *Phys. Stat. Sol. Ser.A*, **12**, 9 (1972).
3. D.Jerome, A.Masaud, M.Ribault et al., *J. Phys. Lett.*, **41**, L95, (1980).
4. M.Tanaka, F.Urano, M.Nakabata, Japan Patent 60-139832 (1987).
5. V.A.Starodub, V.V.Barabashova, Ye.M.Gluzman et al., USSR Patent 1389226 (1987).
6. Sanyo Electric Co., USA Patent No.458055 (1986).
7. V.A.Starodub, Ye.M.Gluzman, K.V.Krikunov et al., USSR Patent 1696428 (1991).

8. V.A.Starodub, Ye.M.Gluzman, K.I.Pokhodnya, M.Ya.Valah, *Theor. Exp. Chem.*, **29**, 361 (1993).
9. V.A.Starodub, Ye.M.Gluzman, Yu.A.Kaftanova, I.Olejniczak, *Theor. Exp. Chem.*, **33**, 111 (1997).
10. T.Sugimoto, K.Ueda, M.Tsujii et al., *Chem. Phys. Lett.*, **249**, 304 (1996).
11. V.A.Starodub, A.V.Kravchenko, A.R.Kazachkov et al., *Functional Materials*, **10**, 739 (2003).
12. SHELXTL-97. Programmpaket: Sheldrick G.M. University Goettingen (1997).
13. T.M.Krycowski, R.Anulewicz, *Acta Cryst.*, **B39**, 732 (1983).
14. D.V.Ziolkovskiy, A.V.Kravchenko, V.A.Starodub et al., *Functional Materials*, **11**, 316 (2004).
15. J.M.Ziman, Models of Disorder, Cambridge University Press: Cambridge, London, New York, Melbourne (1979).

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

Д.В.Зіолковський, А.В.Кравченко, В.О.Стародуб, О.Н.Кажева, А.В. Хоткевич

Визначено кристалічну і молекулярну структуру синтезованої авторами раніше аніон-радикальної солі (АРС) 7,7,8,8-тетраціанохінодиметану (TCNQ) незвичайного складу $[N–(H_5C_2)–Pz](TCNQ)_3$, де Pz — піразин. Структура даної АРС 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 неалкильованого атому азоту піразину. Частки типу *B*, як і частки TCNQ у стопках, мають помітний заряд (близько −0,3). Така особливість структури додає електронній системі АРС певну двомірність, незвичайну для АРС TCNQ, і добре узгоджується з результатами електрофізичних вимірів.