Crystal and molecular structure of the complex radical ionic salt, *N*-(β-iodoethyl)pyridinium bis(7,7′,8,8′-tetracyanoquinodimethanide), $(C_7H_9IN)^+ \cdot (TCNQ)^{\cdot -} \cdot (TCNQ)$

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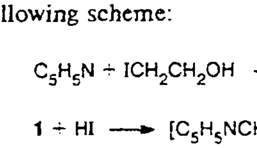
A complex radical ionic salt, *N*-(β-iodoethyl)pyridinium bis(7,7′,8,8′-tetracyanoquinodimethanide), $(C_7H_9IN)^+ \cdot (TCNQ)^{\cdot -} \cdot (TCNQ)$, where TCNQ is 7,7′,8,8′-tetracyanoquinodimethane, was synthesized and studied by X-ray structural analysis. The crystal structure of the complex consists of layers. Layers of $(C_7H_9IN)^+$ cations alternate with layers of TCNQ molecules packed in stacks. Shortened intermolecular contacts occur in stacks of TCNQ and between cationic and anionic layers.

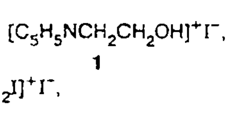
Key words: 7,7′,8,8′-tetracyanoquinodimethane, radical ionic salt, synthesis, molecular and crystal structure; intermolecular interactions.

It is known that the physical properties of molecular conductors are associated with their dimensions and are determined to a large extent by their crystal structures.[1] It has been established that different structural variations occur in crystals as a result not only of acceptor—acceptor or donor—donor interactions but of acceptor—cation and donor—anion interactions as well. However even recently, when new molecular conductors were constructed, primarily the geometry and electronic structure of starting molecules rather than the crystal structure as a whole (including interactions with counterions) were taken into account.[2] Hydrogen bonds were taken into account only in the salts of 7,7′,8,8′-tetracyanoquinodimethane (TCNQ)[3] and bis(ethylenedithio)tetrafulvalene (BEDT-TTF).[4] However, attempts to fix hydrogen bonds in the orientations necessary for interactions with adjacent molecules were not necessarily successful. Nevertheless, there are many neutral molecules whose crystal packings are determined by strong directed interactions predominating in these crystal structures. The —I...NC— type interaction in the crystal structure of *p*-iodobenzonitrile,[5] which leads to the formation of a one-dimensional chain

$$...IC_6H_4CN...IC_6H_4CN...IC_6H_4CN....$$

is one example. Recently, such interactions were used in the construction of conducting structures based on iodine-substituted tetrathiafulvalenes IEDT and DIET with different CN-containing anions ($C(CN)_3^-$, SCN^-, and $M(CN)_2^-$; M = Au or Ag).[6] In contrast to other halides, the electronegativity of the I atom (2.2) is smaller than that of the C atom (2.5). Therefore, the introduction of an iodine atom does not weaken the donor properties of tetrathiafulvalene and, moreover, makes an additional contribution to the highest occupied molecular orbital (HOMO). For example, in the crystal of the salt $(IEDT)_2Ag(CN)_2$ [6] the I...NC distance between the donor IEDT molecule and the $Ag(CN)_2^-$ anion is 2.88 Å. This distance is substantially smaller than the sum of the van der Waals radii of the bound atoms (3.64 Å)[7] and than the I...N distance (3.18 Å) in the crystal of *p*-iodobenzonitrile,[5] which is indicative of a strong interaction between the I atoms and the CN groups.


IEDT


DIET

Analogous strong interactions can be used also to make desired changes in the packing mode and properties of TCNQ salts because each of its molecules contains four CN groups. We synthesized this salt containing a covalently bound iodine atom according to the following scheme:

$$C_5H_5N + ICH_2CH_2OH \longrightarrow \underset{\mathbf{1}}{[C_5H_5NCH_2CH_2OH]^+I^-},$$

$$\mathbf{1} + HI \longrightarrow \underset{\mathbf{2}}{[C_5H_5NCH_2CH_2I]^+I^-},$$

$$\mathbf{2} + TCNQ \longrightarrow \underset{\mathbf{3}}{[C_5H_5NCH_2CH_2I]^+(TCNQ)^-_2}.$$

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At the first stage pyridine reacted with ethylene iodohydrin to form *N*-(β-hydroxyethyl)pyridinium iodide (**1**). When boiled with hydroiodic acid, compound **1** gave *N*-(β-iodoethyl)pyridinium iodide (**2**). Compound **2** reacted with TCNQ in acetonitrile to form a complex salt, *N*-(β-iodoethyl)pyridinium bis(7,7′,8,8′-tetracyanoquinodimethanide), $(C_7H_9IN)^+ \cdot (TCNQ)^{\cdot -} \cdot (TCNQ)$ (**3**). The cation of this salt contains a covalently bound iodine atom. The composition and the crystal and molecular structure of salt **3** were established by X-ray structural analysis.

Experimental

***N*-(β-Iodoethyl)pyridinium iodide (2).** A mixture of pyridine (0.1 mol) and ethylene iodohydrin (0.1 mol) in alcohol (100 mL) was heated for 20 min. The solvent was evaporated *in vacuo*. A 40% HI solution (200 mL) was added to the *N*-(β-hydroxyethyl)pyridinium iodide obtained, and the reaction mixture was boiled for 2 h. Then the excess acid was distilled off over a period of 2 h. A brown oil crystallized out during storage. The product was purified by rubbing it with cold acetonitrile, filtering it off, and washing it on a filter with acetonitrile (50 mL). Virtually colorless salt **2** was isolated. Salt **2** was recrystallized from methanol as colorless needles. The yield was 27.05 g (73%), m.p. 176—178 °C. Found (%): I, 73.25. $C_7H_9I_2N$. Calculated (%): I, 73.15. ^1H NMR (D_2O), δ: 3.68 (t, 2 H, CH_2); 4.93 (t, 2 H, CH_2); 8.53 (m, 5 H, C_5H_5N).

***N*-(β-Iodoethyl)pyridinium bis(7,7′,8,8′-tetracyanoquinodimethanide) (3).** A hot solution of TCNQ (0.2 g, 1 mmol) in acetonitrile was added to a hot solution (20 mL) of compound **2** (0.286 g, 1 mmol) in acetonitrile. The reaction mixture was kept in the dark overnight. Crystals of **3** were obtained as bright black prisms with a metallic luster. The yield was 0.23 g (45%).

Crystallographic parameters of salt 3: $C_{31}H_{17}IN_9$, M = 642.44, monoclinic system, a = 14.307(3) Å, b = 6.592(3) Å, c = 15.394(3) Å, β = 104.78(2)°, V = 1403.9(7) Å^3, space group *Pc*, Z = 2, d_{calc} = 1.519 g cm^{-3}, $F(000)$ = 638, μ(Cu-Kα) = 9.2 mm^{-1}.

The systematic absences indicated two possible space groups: the centrosymmetric space group *P*2/*c* and the noncentrosymmetric space group *Pc*. Space group *Pc* was chosen because there are two molecules of the complex, namely, two cations and four TCNQ molecules, per asymmetric unit. In space group *Pc*, the multiplicity of a general position is 2, and therefore, one cation and two TCNQ molecules occupy general positions, which is consistent with their local symmetry. In space group *P*2/*c*, the multiplicity of a general position is equal to 4, and the multiplicities of the special positions 2 and $\bar{1}$ are equal to 2, *i.e.*, none of these symmetries corresponds to the possible symmetry of the cation. This unambiguously indicates space group *Pc*, which is of fundamental importance for this structure because it allows one to identify crystallographically independent TCNQ molecules according to charges (according to the distribution of bond lengths).

Crystals of **3** are thin black prisms. X-ray experimental data were collected from a crystal of dimensions 0.42×0.11×0.10 mm. Intensities of 3216 reflections (2941 reflections with $I > 2\sigma(I)$) were measured on an automated four-circle KM-4 diffractometer (Kuma Diffraction, Poland) with the use of monochromated Cu-Kα radiation using the ω/2θ scanning technique in the range 3.19° < θ < 80.54°. The structure was solved by the direct method and refined by the least-squares method with anisotropic thermal parameters for nonhydrogen atoms to R = 0.078 using the weighting scheme $w = 1/[\sigma^2(F_{\text{exp}})^2 + (0.002P)^2 + 4000P]$, where $P = [\max/(F_{\text{exp}})^2 + (2F_{\text{calc}})^2]/3$. The positions of H atoms were calculated geometrically.

The atomic coordinates and thermal parameters are given in Table 1. The bond lengths and bond angles in the structure of **3** are given in Table 2.

All calculations were carried out on a PC AT-486 computer using the SHELXS-86 [8] and SHELXL-93 [9] program packages.

Table 1. Coordinates of nonhydrogen atoms (×10^4) and their equivalent isotropic thermal parameters (U_{eq}×10^3) in the structure of **3**

Atom	x	y	z	U_{eq}/Å^2
I	272(1)	2202(1)	1325(1)	183(1)
N(1)	−1090(2)	6977(7)	−400(2)	81(1)
N(2)	5269(2)	−872(6)	7811(2)	60(1)
N(3)	6965(2)	−1138(6)	5901(2)	56(1)
N(4)	1923(3)	−1762(8)	1710(2)	88(2)
N(5)	184(3)	−1798(6)	3646(3)	82(2)
N(6)	6526(2)	4225(7)	8786(2)	68(1)
N(7)	8156(2)	3852(7)	6794(2)	64(1)
N(8)	3173(2)	3488(7)	2604(2)	68(1)
N(9)	1389(2)	3533(6)	4435(2)	67(1)
C(1)	−979(3)	6909(8)	−1245(3)	65(2)
C(2)	−1485(3)	8173(7)	−1882(2)	54(1)
C(3)	−2175(3)	9375(7)	−1704(3)	56(1)
C(4)	−2294(3)	9461(7)	−868(3)	71(1)
C(5)	−1775(3)	8313(8)	−237(3)	70(2)
C(6)	−387(4)	5924(11)	408(4)	98(2)
C(7)	−818(4)	3869(11)	275(4)	102(2)
C(8)	4416(2)	−1253(5)	5464(2)	33(1)
C(9)	4443(2)	−1296(5)	4522(2)	34(1)
C(10)	3644(2)	−1400(5)	3876(2)	34(1)
C(11)	2707(2)	−1477(5)	4064(2)	36(1)
C(12)	2664(2)	−1398(5)	4979(2)	38(1)
C(13)	3479(2)	−1267(5)	5635(2)	37(1)
C(14)	5246(2)	−1157(5)	6142(2)	36(1)
C(15)	1875(3)	−1646(6)	3374(2)	48(1)
C(16)	5228(2)	−1008(6)	7067(2)	47(1)
C(17)	6207(2)	−1163(5)	5983(2)	38(1)
C(18)	1916(3)	−1753(7)	2447(3)	58(1)
C(19)	941(3)	−1693(6)	3534(3)	50(1)
C(20)	3928(2)	3657(5)	4965(2)	35(1)
C(21)	4885(2)	3682(5)	4813(2)	37(1)
C(22)	5680(2)	3789(5)	5495(2)	36(1)
C(23)	5650(2)	3905(5)	6414(2)	34(1)
C(24)	4710(2)	3901(5)	6581(2)	36(1)
C(25)	3883(2)	3772(5)	5887(2)	38(1)
C(26)	6491(2)	4012(5)	7108(2)	36(1)
C(27)	3109(2)	3594(5)	4261(2)	34(1)
C(28)	6452(2)	4108(6)	8030(2)	45(1)
C(29)	7404(3)	3951(6)	6932(2)	45(1)
C(30)	3155(3)	3535(6)	3342(2)	49(1)
C(31)	2159(2)	3554(6)	4378(2)	45(1)

Table 2. Bond lengths (*d*) and bond angles (ω) in the structure of 3 (see Fig. 2)

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
I—C(7)	2.228(6)	C(15)—C(18)	1.446(6)	N(1)—C(1)—C(2)	120.5(4)	C(11)—C(15)—C(19)	122.1(3)
N(1)—C(1)	1.351(6)	N(4)—C(18)	1.136(5)	C(1)—C(2)—C(3)	120.0(4)	C(18)—C(15)—C(19)	116.6(3)
C(1)—C(2)	1.349(6)	C(15)—C(19)	1.420(6)	C(2)—C(3)—C(4)	120.0(4)	N(4)—C(18)—C(15)	176.9(5)
C(2)—C(3)	1.347(6)	N(5)—C(19)	1.141(6)	C(3)—C(4)—C(5)	120.2(4)	N(5)—C(19)—C(15)	177.4(5)
C(3)—C(4)	1.342(6)	C(20)—C(21)	1.448(4)	C(1)—N(1)—C(5)	117.2(4)	C(20)—C(21)—C(22)	121.6(3)
C(4)—C(5)	1.303(6)	C(21)—C(22)	1.339(4)	C(5)—N(1)—C(6)	118.9(4)	C(21)—C(22)—C(23)	123.0(3)
N(1)—C(5)	1.388(6)	C(22)—C(23)	1.428(4)	C(1)—N(1)—C(6)	123.1(4)	C(22)—C(23)—C(24)	116.5(2)
N(1)—C(6)	1.549(6)	C(23)—C(24)	1.432(4)	N(1)—C(6)—C(7)	97.9(4)	C(23)—C(24)—C(25)	121.3(3)
C(6)—C(7)	1.480(10	C(24)—C(25)	1.379(4)	I—C(7)—C(6)	99.3(3)	C(20)—C(25)—C(24)	121.5(3)
C(8)—C(9)	1.461(4)	C(20)—C(25)	1.439(5)	C(8)—C(9)—C(10)	121.0(3)	C(21)—C(20)—C(25)	116.1(2)
C(9)—C(10)	1.311(4)	C(23)—C(26)	1.392(4)	C(9)—C(10)—C(11)	121.6(3)	C(22)—C(23)—C(26)	121.6(3)
C(10)—C(11)	1.442(5)	C(26)—C(28)	1.435(5)	C(10)—C(11)—C(12)	118.3(2)	C(24)—C(23)—C(26)	121.9(3)
C(11)—C(12)	1.427(5)	N(6)—C(28)	1.144(5)	C(11)—C(12)—C(13)	119.9(3)	C(23)—C(26)—C(28)	121.1(3)
C(12)—C(13)	1.337(4)	C(26)—C(29)	1.401(5)	C(8)—C(13)—C(12)	122.7(3)	C(23)—C(26)—C(29)	121.0(3)
C(8)—C(13)	1.431(5)	N(7)—C(29)	1.151(5)	C(9)—C(8)—C(13)	116.4(2)	C(28)—C(26)—C(29)	117.8(3)
C(8)—C(14)	1.368(4)	C(20)—C(27)	1.378(4)	C(9)—C(8)—C(14)	121.4(3)	N(6)—C(28)—C(26)	172.6(4)
C(14)—C(16)	1.435(5)	C(27)—C(30)	1.434(5)	C(13)—C(8)—C(14)	122.1(3)	N(7)—C(29)—C(26)	178.3(4)
N(2)—C(16)	1.135(5)	N(8)—C(30)	1.144(5)	C(8)—C(14)—C(16)	121.9(3)	C(21)—C(20)—C(27)	121.5(3)
C(14)—C(17)	1.456(5)	C(27)—C(31)	1.416(5)	C(8)—C(14)—C(17)	123.0(3)	C(25)—C(20)—C(27)	122.3(3)
N(3)—C(17)	1.123(5)	N(9)—C(31)	1.128(5)	C(16)—C(14)—C(17)	115.1(3)	C(20)—C(27)—C(30)	122.2(3)
C(11)—C(15)	1.383(4)			N(2)—C(16)—C(14)	176.0(4)	C(20)—C(27)—C(31)	123.4(3)
				N(3)—C(17)—C(14)	176.7(3)	C(30)—C(27)—C(31)	114.4(3)
				C(10)—C(11)—C(15)	120.7(3)	N(8)—C(30)—C(27)	178.7(4)
				C(12)—C(11)—C(15)	121.1(3)	N(9)—C(31)—C(27)	177.2(4)
				C(11)—C(15)—C(18)	121.3(4)		

Results and Discussion

The crystal structure of complex 3 (Fig. 1) consists of a $(C_7H_9IN)^+$ cation and two crystallographically independent TCNQ molecules (denoted by **A** and **B**). The overall view of the cation and the TCNQ molecules and the atomic numbering scheme are shown in Fig. 2. The structure of salt 3 consists of layers. Layers of $(C_7H_9IN)^+$ cations alternate with layers of TCNQ molecules along the *a* axis. The layers are parallel to the *bc* plane.

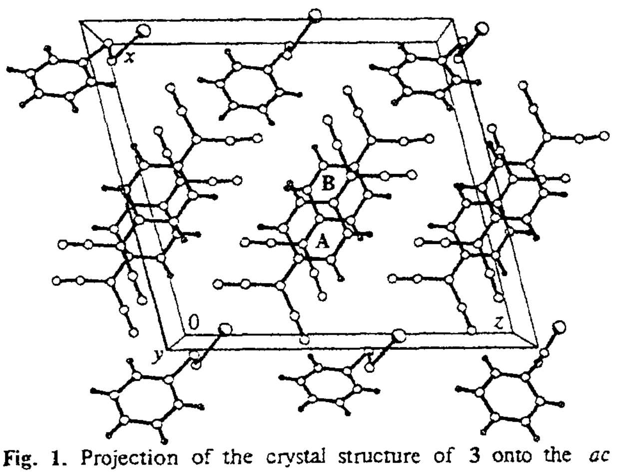


Fig. 1. Projection of the crystal structure of 3 onto the *ac* plane.

In the anionic layer, TCNQ molecules are packed in infinite stacks parallel to the *b* axis. The mode of overlapping of the adjacent molecules in the stack is shown in Fig. 3. TCNQ molecules are shifted with respect to each other so that the center of the six-membered ring of one molecule is located above the middle of the quinoid double bond of the other molecule.

In stacks, TCNQ molecules are virtually parallel to each other (the dihedral angle is 1.2°). The interplanar TCNQ...TCNQ distances between the adjacent molecules are nearly identical (3.28 and 3.30 Å). Shortened intermolecular C...C contacts (3.300(5)—3.395(5) Å) are observed only in stacks (Table 3). Substantially shortened van der Waals contacts occur between the cationic and anionic layers (the I...N(4) and I...C(18) distances are 3.471(5) and 3.639(4) Å, respectively). The fact that the I—C(7) bond [2.228(6) Å] is substantially longer than the sum of the van der Waals radii of these atoms (2.05 Å) is attributable to the participation of the I atom in secondary interactions with the N(4) and C(18) atoms. It is also possible that the anomalously large thermal parameters of the I atom are determined by its disorder. The refinement of the structure taking into account the positional disorder of the I atom gave two positions, I(1) and I(2), with occupancies of 0.8 and 0.2, respectively, and resulted in an increase in the *R* factor to 0.087. The values of the I(1)—C(7) and I(2)—C(7) bond lengths [2.318(7) and 2.650(8) Å, respectively] and the I(1)—C(7)—C(6) and I(2)—C(7)—C(6) bond angles [98.2(4)° and 79.3(4)°, respectively] obtained in

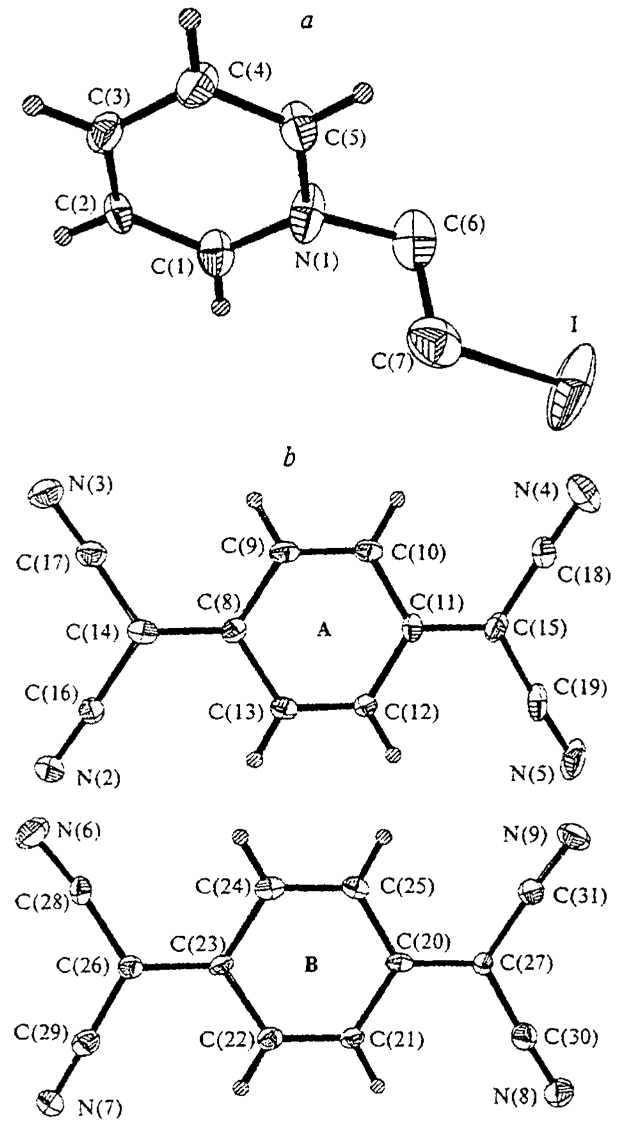


Fig. 2. Molecular structure of the $(C_7H_9IN)^+$ cation (*a*) and two crystallographically independent TCNQ molecules **A** and **B** (*b*).

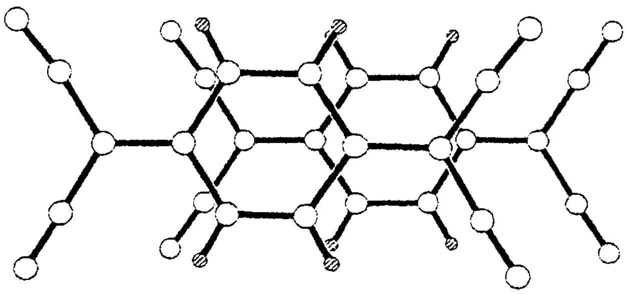


Fig. 3. Mode of overlapping of adjacent TCNQ molecules in stacks of complex **3**.

Table 3. Intermolecular contacts (*D*) shorter than the sums of the van der Waals radii[7] (I...N < 3.64 Å, I...C < 3.85 Å, and C...C < 3.42 Å)

Contact	*D*/Å	Contact	*D*/Å
I...N(4)	3.471(5)	C(11)...C(27)*	3.300(5)
I...C(18)	3.639(4)	C(13)...C(25)	3.378(5)
C(8)...C(20)	3.359(5)	C(13)...C(25)*	3.326(5)
C(9)...C(21)	3.350(5)	C(14)...C(23)	3.395(5)
C(9)...C(21)*	3.379(5)	C(14)...C(23)*	3.314(5)
C(10)...C(30)	3.385(5)	C(17)...C(22)	3.392(5)
C(11)...C(27)	3.393(5)		

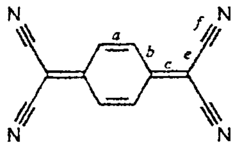
* *x*, −1 + *y*, *z*.

this case cast some doubt on the occurrence of such conformers of *N*-(β-iodoethyl)pyridinium.

The $(C_7H_9IN)^+$ cation (see Fig. 2, *a*) is nonplanar. The dihedral angle between the planar (within ±0.05 Å) IC(7)C(6)N(1) fragment and the plane of the heterocycle is 80.8°. The TCNQ molecules are planar to within ±0.07 Å and are located almost parallel to the *ac* plane. The dihedral angles between the planes of the TCNQ molecules and the *ac* plane of the lattice are 3.56° and 3.04° for molecules **A** and **B**, respectively.

The average bond lengths in TCNQ molecules **A** and **B** are given in Table 4. The analogous parameters of the neutral TCNQ molecule and the radical anion $(TCNQ)^{\cdot-}$ are also given in Table 4. A comparison of the corre-

Table 4. Average bond lengths (*d*) in the TCNQ molecules **A** and **B**, the neutral molecule TCNQ, and the radical anion $(TCNQ)^{\cdot-}$



Structure	*d*/Å					Reference
	a	*b*	*c*	*e*	*f*	
TCNQ (**A**)	1.324(4)	1.440(5)	1.376(4)	1.439(6)	1.134(6)	This work
TCNQ (**B**)	1.359(4)	1.437(5)	1.385(4)	1.422(5)	1.142(5)	This work
TCNQ	1.346(0)	1.448(2)	1.374(0)	1.440(1)	1.140(1)	10
$(TCNQ)^{\cdot-}$	1.367(12)	1.426(15)	1.415(13)	1.418(12)	1.150(5)	11

sponding bond lengths suggests that, according to the character of their distribution, **A** is a neutral molecule and **B** is a radical anion. Complex **3** is a complex radical anionic salt $(C_7H_9IN)^+ \cdot (TCNQ)^{\cdot -} \cdot (TCNQ)$.

According to the published data,[11] the above-mentioned characteristic feature of the crystal structure of complex 3, namely, formation of infinite stacks of TCNQ with virtually identical interplanar TCNQ—TCNQ distances and the same mode of overlapping of the adjacent TCNQ molecules and anions throughout the stack, is typical of high-conductivity compounds of tetracyanoquinodimethane.

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