

# Crystal and Molecular Structure of Anion Radical Salt (N-Me-DABCO)(TCNQ)<sub>2</sub>

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**Abstract**—An anion radical salt of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with the complex composition (N-Me-DABCO)(TCNQ)<sub>2</sub> (**1**) has been synthesized. The crystal structure **1** has been characterized by X-ray diffraction. The structure of this salt consists of almost homogeneous stacks of TCNQ particles separated by cation layers. Interplanar spacings of 3.25 and 3.29 Å alternate in the stacks. Due to the alternating distances and uniform charge distribution in the stacks, conducting channels are formed in the structure, which determine the properties of an organic metal or a narrow-gap semiconductor, as confirmed by IR spectra containing electron-phonon interaction-related features. In particular, vibrational lines against the continuous absorption background are observed: the band gap does not exceed 0.06 eV. As a result lines of totally symmetric vibrations appear (without the electron-phonon interaction, these lines are forbidden in the IR spectra).

## INTRODUCTION

Anion radical salts (ARSs) based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) have attracted interest since the 1960s [1, 2]. The attention to the TCNQ ARS is due to their extraordinary properties: the first organic metals were found among them; TCNQ ARS can melt without decomposition, which opens up wide opportunities for use of organic conductors, e.g., in production of batteries with solid electrolytes [3, 4]; and TCNQ ARS can be used to create ultrathin films. These ARSs can be used in production of electronic devices of molecular sizes [5]; conductive TCNQ ARS can provide high-efficiency transitions in silicon semiconductors or cadmium sulfide-based semiconductor

devices [6]. The use for the synthesis of ARS TCNQ of cations, which contain donor atoms capable of forming intermolecular bonds, in the ARS synthesis, allows one to synthesize conductive TCNQ ARS and spin ladders [7, 8].

The use of one of these cations, specifically, 1,4-diazabicyclo[2.2.2]octane (DABCO), and its reaction with para-bis(dicyanomethyl)benzene (H<sub>2</sub>TCNQ) were described in [9]. During this reaction, colorless crystals of a salt containing dianion TCNQ<sup>2-</sup> and supramolecular cation [(DABCO-H)<sub>2</sub>DABCO]<sup>2+</sup> are formed (Fig. 1). Note that, in this case, TCNQH<sub>2</sub> behaves as a C-H acid, and DABCO behaves as a proton acceptor (base).

To expand the data, a new TCNQ ARS with a DABCO-based cation was studied; the results of structural and optical measurements are reported. The use of this cation is also interesting, since DABCO forms 2 : 1 crystalline adduct with hydrogen peroxide and sulfur dioxide, is a quencher of singlet oxygen and an effective antioxidant, and can be used to improve the quality of dyes. DABCO is applied in lasers and in

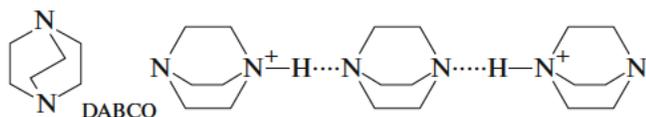


Fig. 1. DABCO and its supramolecular cation [(DABCO-H)<sub>2</sub>DABCO]<sup>2+</sup>.

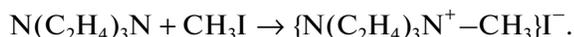
**Table 1.** Crystallographic characteristics, experimental data, and refining results of structure **1**

Chemical formula	C <sub>31</sub> H <sub>23</sub> N <sub>10</sub>
System, sp. gr., <i>Z</i>	Triclinic, <i>P</i> , 1
<i>T</i> , K	180
<i>a</i> , <i>b</i> , <i>c</i> , Å	7.36 (1), 7.55 (1), 13.765 (2)
$\alpha$ , $\beta$ , $\gamma$ , deg	92.3 (1), 92.60 (14), 117.46 (14)
<i>V</i> , Å <sup>3</sup>	677.49 (2)
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.313
$\mu$ , mm <sup>-1</sup>	0.084
Sample size, mm	0.18 × 0.04 × 0.03
Radiation; $\lambda$ , Å	MoK $\alpha$ ; 0.71073
Diffractometer	Stoe StadiVari
Scanning type	$\omega$
2 $\theta$ <sub>max</sub> , deg	56
Number of reflections: measured, <i>R</i> <sub>int</sub> /independent with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	5621, 0.026/3155
<i>R</i> <sub>sigma</sub>	0.060
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.095/0.314
$\Delta\rho_{\min}/\Delta\rho_{\max}$ , e/Å <sup>3</sup>	-0.61/1.62
Programs	SHELXS [12], SHELXTL [13]

fluorescence microscopy for sample fixation (in combination with glycerol) [10].

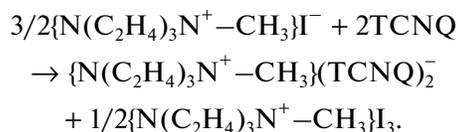
## EXPERIMENTAL

In this study, Aldrich TCNQ was additionally cleaned by recrystallization. (N-*Me*-DABCO)<sup>+</sup>I<sup>-</sup> salt was synthesized according to the reaction



For this purpose, *Me*I (4.18 g, 29.4 mmol) was added in portions to a boiling solution of DABCO (3.00 g, 26.7 mmol) in 10 mL of methyl tert-butyl ether (MTBE) and 10 mL of isopropanol *i-Pr*OH. The obtained mixture was stirred for 30 min using a reflux condenser. A yellowish precipitate was filtered off, washed twice with 20-mL portions of the mixture (1 : 1) MTBE:*i-Pr*OH, and dried in air. The yield of the yellow crude product was 5.10 g (75%). It was recrystallized from methanol (cooled, filtered off, and washed with three 5-mL portions of acetone) until colorless crystals of the product (3.12 g, 46%) were obtained. The <sup>1</sup>H NMR data are consistent with the data from [11].

The ARS was synthesized using the reaction



Hot solutions of {N(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>N<sup>+</sup>-CH<sub>3</sub>}I<sup>-</sup> and TCNQ in acetonitrile were mixed and placed in a Dewar flask for slow cooling. After a week, dark green crystals formed, which were separated, washed with cold acetonitrile and diethyl ether, and dried in air.

The ARS composition was determined spectrophotometrically, as described in [7]. It corresponds to the formula {N(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub>N<sup>+</sup>-CH<sub>3</sub>} (TCNQ)<sub>2</sub><sup>-</sup> (**1**). The elemental analysis of the synthesized ARS performed using a VarioMICRO Superuser analyzer revealed C 69.43, N 26.30, and H 4.42 wt %. The calculated data for C<sub>31</sub>H<sub>23</sub>N<sub>10</sub> are C 69.52, N 26.15, and H 4.33 wt %. The melting point is 217°C.

The X-ray study of **1** was carried out on a Stoe StadiVari single-crystal diffractometer at 180 K (multi-layer optics, the rotating crystal method). The spherical absorption was corrected using a STOE Lana scaling tool. The structure was solved by direct methods with subsequent building of a difference Fourier synthesis using the SHELXS software [12] and refined by the full-matrix least squares method in the anisotropic approximation of displacements of all TCNQ anion atoms, except for hydrogen, using the SHELXTL software [13].

The cation is disordered over two identically occupied sites. The disordered parts are symmetric with respect to the inversion center. Therefore, all atoms forming the cation, except for hydrogen atoms, were refined in the isotropic approximation of displacements; in addition, restrictions were imposed on the bond lengths N-C<sub>sp</sub><sup>3</sup> (1.47 Å) and C<sub>sp</sub><sup>3</sup>-C<sub>sp</sub><sup>3</sup> (1.54 Å). The positions of hydrogen atoms were determined from difference electron density maps and refined in the isotropic approximation for the TCNQ anion. The hydrogen atoms in the cation were placed in idealized positions and refined according to the riding model with *U*<sub>iso</sub> = *nU*<sub>eq</sub> (*n* = 1.5 for the methyl group and *n* = 1.2 for other hydrogen atoms) of the carrier atom.

The main crystallographic and experimental data are listed in Table 1. The bond lengths and angles are listed in Tables 2 and 3.

The IR absorption spectra of powder samples of **1** were recorded in the frequency range from 500 to 4000 cm<sup>-1</sup> at room temperature on a Nicolet 380 spectrometer, KBr disk.

## RESULTS AND DISCUSSION

The studied salt is formed by two TCNQ anion radicals and the N-*Me*-DABCO cation (Fig. 2). The anion radical is almost flat, and all of its atoms lie

**Table 2.** Bond distances in structure **1**

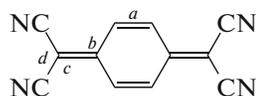
Bond	Length, Å	Bond	Length, Å
N1–C8	1.141(4)	C7–C9	1.438(4)
N2–C9	1.142(4)	C10–C11	1.429(5)
N3–C11	1.139(4)	C10–C12	1.419(5)
N4–C12	1.150(5)	N5–C13	1.337(9)
C1–C2	1.432(4)	N5–C14	1.531(9)
C1–C6	1.435(4)	N5–C16	1.512(9)
C1–C7	1.388(4)	N5–C18	1.468(10)
C2–C3	1.354(5)	N6–C15	1.541(9)
C3–C4	1.440(4)	N6–C17	1.476(9)
C4–C5	1.425(4)	N6–C19	1.492(9)
C4–C10	1.403(4)	C14–C15	1.436(10)
C5–C6	1.353(4)	C16–C17	1.507(11)
C7–C8	1.423(5)	C18–C19	1.533(10)

within a plane accurate to 0.05 Å. The cation is located in a special position with respect to the symmetry center and disordered over two identically occupied sites.

In ARS crystals **1**, cation and anion layers can be distinguished (Fig. 3). The anion layers are formed by stacks in which TCNQ molecules are linked by stacking interactions. The stacking interactions of a TCNQ molecule with two neighboring molecules inside the stack are different (Fig. 4). Cations and anions are linked by very weak hydrogen bonds: C(18)–H(18*b*)⋯N(4) ( $x, y, 1 + z$ ; H⋯N 2.62 Å, C–H⋯N 151°); C(17)–H(17*a*)⋯N(1) ( $x - 1, y - 1, z$ ; H⋯N 2.60 Å, C–H⋯N 99°); and C(13)–H(13*c*)⋯N(4) ( $-x, 1 - y, 1 - z$ ; H⋯N 2.39 Å, C–H⋯N 117°).

As follows from the formula of ARS **1**, the average charge on a TCNQ particle is  $-1/2e$ . The charge can be estimated from the structural data: if the charge on a TCNQ<sup>-*q*</sup> particle decreases, the structure changes from quinoid to aromatic. In this case, the C–C bond length naturally changes.

Kistenmacher [14, 15] proposed a formula that gives the opportunity to calculate the charge of the

**Scheme 1.** Parameters used in the Kistenmacher equation.**Table 3.** Valence angles in structure **1**

Bond	Angle, deg	Bond	Angle, deg
C2–C1–C6	117.6(3)	N3–C11–C10	178.8(4)
C7–C1–C2	121.3(3)	N4–C12–C10	178.7(4)
C7–C1–C6	121.1(3)	C13–N5–C14	116.4(11)
C3–C2–C1	121.1(3)	C13–N5–C16	103.3(10)
C2–C3–C4	121.0(3)	C13–N5–C18	121.7(11)
C5–C4–C3	117.9(3)	C16–N5–C14	102.8(6)
C10–C4–C3	121.2(3)	C18–N5–C14	103.5(6)
C10–C4–C5	120.9(3)	C18–N5–C16	107.2(7)
C6–C5–C4	121.0(3)	C17–N6–C15	106.6(6)
C5–C6–C1	121.4(3)	C17–N6–C19	107.6(6)
C1–C7–C8	122.0(3)	C19–N6–C15	105.4(6)
C1–C7–C9	122.6(3)	C15–C14–N5	117.0(7)
C8–C7–C9	115.4(3)	C14–C15–N6	110.5(6)
N1–C8–C7	178.8(4)	C17–C16–N5	113.3(7)
N2–C9–C7	178.8(4)	N6–C17–C16	112.7(7)
C4–C10–C11	121.7(3)	N5–C18–C19	114.0(7)
C4–C10–C12	122.3(3)	N6–C19–C18	111.3(7)
C12–C10–C11	116.0(3)		

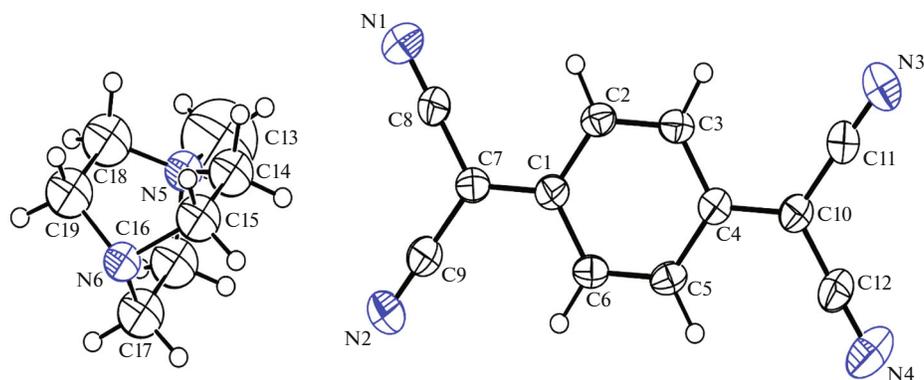
TCNQ molecule based on bond lengths (Table 2) *b*, *c*, and *d* in a TCNQ particle:

$$q = -41.67[c/(b + d)] + 19.83.$$

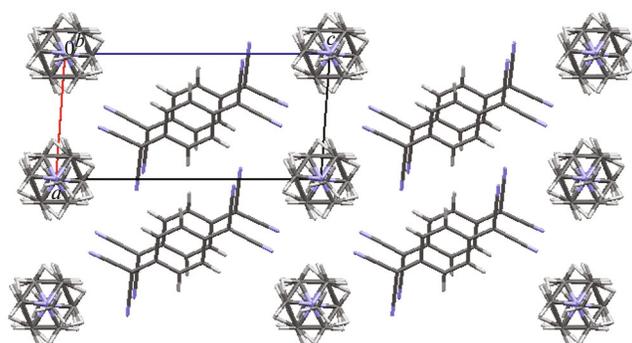
Using data on bond lengths in ARS **1** (Table 2), we obtained the charge of a TCNQ particle in ARS **1**:  $q = -0.43e$ .

In the ARS with the composition  $\text{Kt}^+(\text{TCNQ}^{\bullet-})_2$ , the TCNQ stacks are usually tetramerized due to the Peierls instability [1]. Taking into account that the stacks in ARS **1** are homogeneous, it should have the properties of an organic metal. The Peierls transition must occur at low temperatures. As can be seen in Fig. 2, ARS **1** should be highly anisotropic, because the TCNQ stacks are separated by layers of cations that do not form short contacts with anion radicals.

The conclusion about the high electrical conductivity of ARS **1** is confirmed by the IR spectroscopy data (Fig. 5). As is known [16, 17], the TCNQ ARS is characterized by the strong interaction of conduction electrons with intramolecular phonons. This interaction determines some features in the IR spectra of the TCNQ salts, in particular, anomalously broad high-intensity absorption lines in the ranges of 500, 1100–1300, and 2100–2200  $\text{cm}^{-1}$  are in the IR spectrum of salt **1** (Fig. 5). In the spectrum of ARS **1**, the continu-

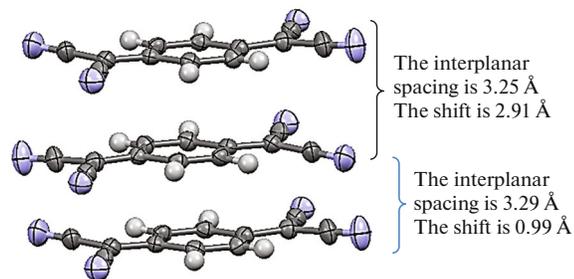


**Fig. 2.** Structures of molecules of the TCNQ<sup>•-</sup> anion radical and N-Me-DABCO cation according to the XRD data. Thermal ellipsoids for TCNQ are drawn at the 50% probability level.



**Fig. 3.** Cation and anion packing in crystals **1**. Projection along the [010] crystallographic direction.

ous radiation absorption is observed over the entire investigated range against the background of the electron-phonon interaction, which activates the totally symmetric vibrations (type  $A_g$ ) allowed only in Raman spectra. The beginning of continuous absorption in the IR spectrum of salt **1** ( $500\text{ cm}^{-1}$ ) makes it possible to estimate the band gap ( $h\nu_0 = \Delta$ , where  $\nu_0$  is the beginning of the permanent absorption and  $\Delta$  is the band gap) as 0.06 eV. Thus, ARS **1** is either an organic metal or a narrow-gap semiconductor.

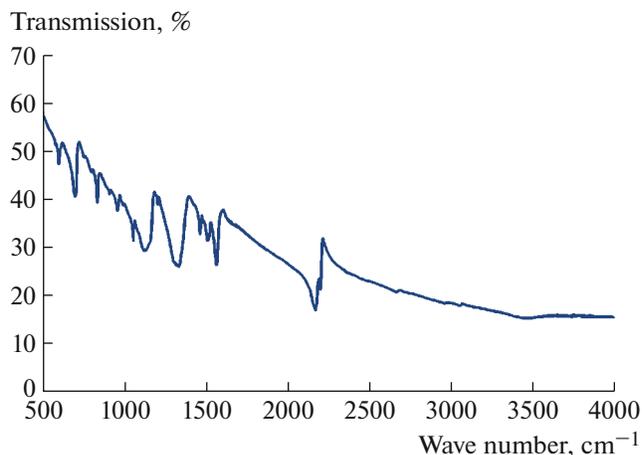


**Fig. 4.** Relative positions of anion radicals in the stacks.

## CONCLUSIONS

A new TCNQ anion radical salt with an alicyclic diamine was synthesized, which contains almost uniform stacks of TCNQ molecules. These stacks are practically isolated. According to the theory of one-dimensional systems, tetramerization should occur in the stacks. However, the X-ray diffraction data show that the tetramerization of the stacks is very weak. The structure of crystals **1** facilitates the formation of the conducting state of the salt, which is confirmed by the IR spectroscopy data. The use of an organic cation N-Me-DABCO or other DABCO-based cations as a counterion may lead to the occurrence of new organic conductors based on the ARS TCNQ.

The final atomic coordinates and crystallographic data for ARS **1** were deposited at the Cambridge Crystallographic Center, 12 Union Road, CB2 1EZ, UK (fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk) and are available upon request with indication of CCDC 2007582.



**Fig. 5.** IR spectrum of ARS **1**.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Bondareva