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7,7,8,8-Tetracyanoquinodimethane in Addition, Substitution, and Complex Formation Reactions

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The review is devoted to the properties of 7,7,8,8-tetracyanoquinodimethane, one of the strongest of the known organic π acids. Data concerning the methods of synthesis of 7,7,8,8-tetracyanoquinodimethane and its analogues and the physicochemical properties of compounds of this series are surveyed. The addition, substitution, and complex formation reactions of 7,7,8,8-tetracyanoquinodimethane, its spectroscopic, electrical, and magnetic properties, and the structures of its complexes and radical-ion salts with organic and inorganic electron donors are examined.
The bibliography includes 232 references.

CONTENTS

I. Introduction 1091
II. The synthesis of 7,7,8,8-tetracyanoquinodimethane and its analogues and their physicochemical properties 1091
III. Chemical properties 1093
IV. Physicochemical properties of 7,7,8,8-tetracyanoquinodimethane complexes 1098

I. INTRODUCTION

The semiconducting properties of molecular complexes or charge-transfer complexes have been widely investigated in the last 20 years. Although organic semiconductors have not so far found extensive practical applications, in contrast to inorganic semiconductors, interest in these compounds has been stimulated by the synthesis of several new powerful electron acceptors, such as tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and tetracyano-*p*-benzoquinone. Although the first two compounds are somewhat inferior as regards their electron-accepting properties to the last, their comparatively easy synthesis led to a vigorous investigation of their chemical properties as well as the physical properties of their complexes.

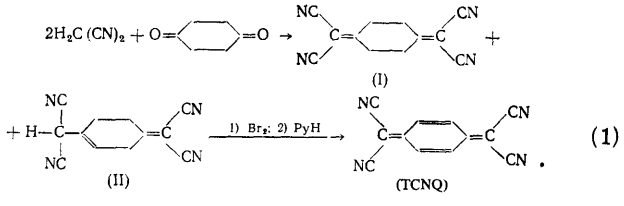
In this connection TCNQ is of particular interest. As a result of the presence in its molecule of four powerful electron-accepting groups, nucleophilic addition reactions, which are rarely encountered among unsaturated compounds, as well as addition reactions proceeding via a one-electron transfer stage are characteristic of this substance. The addition reactions are particularly interesting from the standpoint of modern ideas on the mechanisms of heterolytic substitution reactions. As a result of its powerful electron-accepting properties combined with a comparatively large conjugation system in the molecule (eight π electrons), TCNQ forms a stable radical-anion and gives rise to stable radical-ion salts with many organic and inorganic electron donors, some of which exhibit the highest electrical conductivity observed for organic compounds.

Several TCNQ radical-anion compounds exhibiting "a metallic" temperature variation of the electrical conductivity have been synthesised in recent years. In order to account for the conduction mechanism in such systems, the most modern and fundamental ideas of solid state physics have been resorted to. Thus TCNQ has been the object of intense study by workers in both chemistry and physics.

So far there has been no review dealing with the entire wide variety of properties of both TCNQ itself and its complexes; several of the published reviews deal only with narrow questions concerning the properties of TCNQ complexes. The bibliography on TCNQ and its complexes includes about 600 items. The present review covers the most interesting data relevant to the methods of synthesis and the physicochemical properties of TCNQ and its analogues as well as complexes and radical-ions based on them, which have been published up to the beginning of 1975. Some of the studies on TCNQ, particularly early ones, have been described in reviews which are referred to in the corresponding sections of the present survey.

II. THE SYNTHESIS OF 7,7,8,8-TETRACYANOQUINODIMETHANE AND ITS ANALOGUES AND THEIR PHYSICOCHEMICAL PROPERTIES

Although the reports about the properties of TCNQ complexes refer to 1960, its synthesis was described for the first time in 1962.[1] In the first stage malononitrile is condensed with cyclohexane-1,4-dione and then TCNQ is obtained by bromination and dehydrobromination in the presence of pyridine (in a single stage) [reaction (1)], the overall yield of the product reaching 80%:

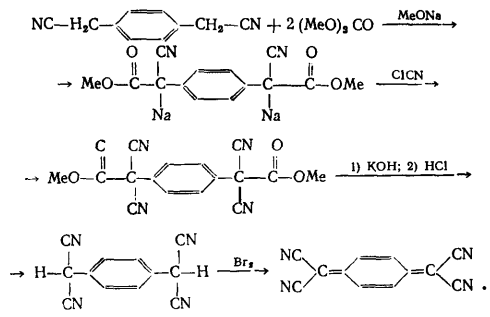


(1)

The first stage may be carried out either in benzene solution in the presence of small amounts of acetic acid and ammonium acetate or in an aqueous medium in the presence of β-alanine. In the first case a mixture of isomers (I) and (II) is formed (this is unimportant for the next stage) in a yield of 75.1%. The second case involves the formation of only isomer (I) in 97% yield. The second stage, the dehydrogenation of compound (I) or a mixture

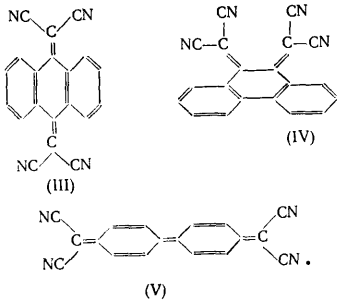
of (I) and (II), may be carried out with the aid of various reagents: *N*-bromosuccinimide, bromine, selenium dioxide, or *N*-chlorosuccinimide; the purest product was obtained by using bromine[1].

Alkyl derivatives of TCNQ were synthesised by a similar procedure: 2-methyl-, 2-propyl-, and 2,5-dimethyl-TCNQ.[2] The starting materials for their synthesis were the alkyl derivatives of cyclohexane-1,4-dione obtained by reducing the corresponding alkyl derivatives of the dimethyl ether of hydroquinone with sodium in liquid ammonia and subsequent demethylation:



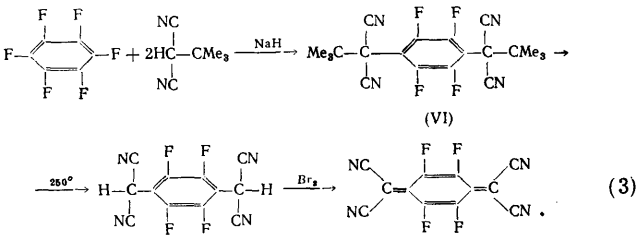
(2)

About 20 TCNQ derivatives with different substituents in the ring (alkyl, alkoxy-, halogeno-, and aryl) have been synthesised by the method based on reaction (2) and on the basis of condensed aromatic hydrocarbons—15,15,16,16-tetracyano-9,10-anthraquinodimethane (III), 15,15,16,16-tetracyano-9,10-phenanthroquinodimethane (IV), and 13,13,14,14-tetracyano-1,12-diphenoquinodimethane (V):[3]



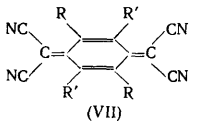
TCNQ was obtained recently (in 80% yields) by the single-stage condensation of cyclohexane-1,4-dione with $(CN)_2CO$ or phosgene in the presence of HCN or NaCN.[4]

The starting materials for the synthesis of 2,3,5,6-tetrafluoro-TCNQ were t-butylmalononitrile and hexafluorobenzene, which in the presence of sodium hydride give rise to the condensation product (VI), the latter being converted into 2,3,5,6-tetrafluoro-TCNQ after hydrolysis and treatment with an excess of bromine [reaction (3)]:[5]



(3)

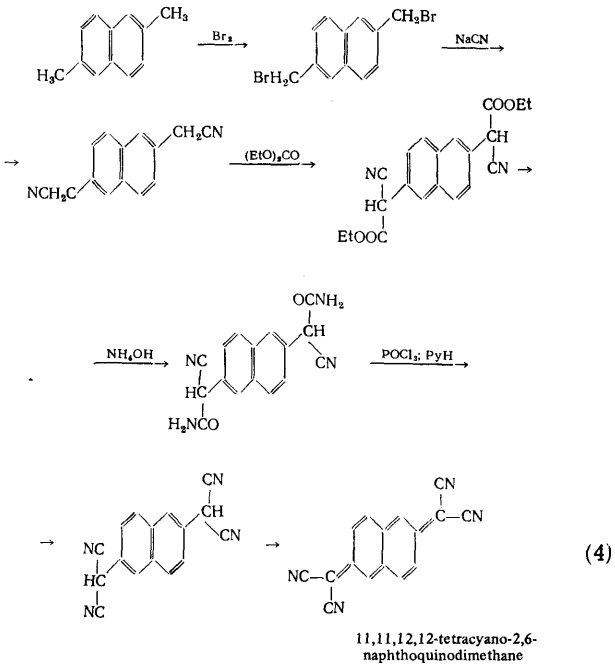
A whole series of substituted TCNQ derivatives (VII) were obtained using polyhalogeno- and cyano-benzenes[5]:



(a) R=H, R'=CN; (b) R=F, R'=CN; (c) R=R'=CN; (d) R=H, R'=F; (e) R=F, CN; R'=F; (f) R=F, CN, R'=CN; (g) R=F, H, R'=F.

Two naphthalene analogues of TCNQ have been synthesised: 11,11,12,12-tetracyano-1,4-naphthoquinodimethane and 11,11,12,12-tetracyano-2,6-naphthoquinodimethane. The former was obtained from *cis*-2,3,5,8,9,10-hexahydro-1,4-naphthoquinone via reaction (1).[6]

The synthesis of 11,11,12,12-tetracyano-2,6-naphthoquinodimethane is much more complex [reaction (4)].[2] The starting material for this purpose was 2,6-dimethylnaphthalene into which four CN groups were introduced in succession: the abstraction of two methine hydrogen atoms led to a common system of conjugated double bonds in the molecule. 11,11,12,12-Tetracyano-2,6-naphthoquinodimethane was synthesised recently also via reaction (2) and the method of preparation of the initial 2,6-naphthylenedimalononitrile was considerably improved[7]:



(4)

11,11,12,12-tetracyano-2,6-naphthoquinodimethane

The interaction of diphenyldiazomethane with TCNQ leads to 2-diphenylmethyl-TCNQ.[8]

Data on the electron-accepting capacity of TCNQ, its analogues, and derivatives (and for comparison of TCNE[9]) are presented in Table 1. The principal characteristic of the strength of the acceptor is its electron affinity E_A. The values of E_A for TCNQ and TCNE, determined by the magnetron method, are 2.75 and 2.76 eV respectively[10].

Another widely used method for the determination of E_A is based on the proportionality of the electron affinity of the acceptor to the half-wave potential in its polarographic titration. The E_A for 11,11,12,12-tetracyano-1,4- and 11,11,12,12-tetracyano-2,6-naphthoquinodimethanes were determined in this way[6]. Since there are no E_A values in the literature for the remaining acceptors, we quote here the literature data for polarographic titration under standard conditions: in 0.1 M lithium perchlorate solution in acetonitrile relative to the saturated calomel electrode.

It follows from the data in Table 1 that the introduction of fluorine or the CN group enhances sharply the electron-accepting properties of TCNQ. Alkyl derivatives of TCNQ as well as 11,11,12,12-tetracyano-1,4-naphthoquinodimethane are clearly weaker electron acceptors (particularly the latter) than TCNQ itself. According to X-ray diffraction data, the CN groups in 11,11,12,12-tetracyano-1,4-naphthoquinodimethane are not in the same plane as the naphthalene ring owing to the steric interaction with the hydrogen atoms in the 5- and 8-positions[11]. In the electronic spectrum of 2-diphenylmethyl-TCNQ the absorption band exhibits a fairly considerable hypsochromic shift (Table 1), which indicates a non-planar conformation of its molecule. However, all the TCNQ derivatives listed in Table 1 are fairly powerful electron acceptors and form complexes and radical-ion salts with organic and inorganic electron donors[2,6]. Since all the electron acceptors have similar structures, we shall henceforth consider only TCNQ, because investigators have concentrated attention on its properties and those of its complexes.

Table 1. The properties of TCNQ and its derivatives ($E_{1/2}^{-}$ and $E_{1/2}^{=}$ are the half-wave potentials in polarographic titration with formation of an anion and dianion respectively; E_A is the electron affinity).

Acceptor	M.p., °C	$E_{1/2}^{-}$, V	$E_{1/2}^{=}$, V	λ_{max}, nm($10^{-4}\epsilon$)	eV	Refs.
3,6-Dicyano-2,5-difluoro-TCNQ		+0.75	+0.23	—	—	5
2,5-Dicyano-TCNQ		+0.07	+0.07	—	—	5
2,3,5,6-Tetrafluoro-TCNQ	295—300	+0.52	+0.03	—	—	5
11,11,12,12-Tetracyano-2,6-naphthoquinodimethane	>420	+0.21	−0.17	248 (1.8) 258 (1.4) 472 (8.7)	1.65*	2
TCNE	199—200	+0.15	−0.57	265	2.76**	9
TCNQ	296—298	+0.14	−0.29	395 (6.36)	2.75**	1
2,5-Diisopropyl-TCNQ	—	+0.12	−0.38	—	—	2
2-Methyl-TCNQ	200—201	+0.12	−0.26	396 (6.0)	—	2
2-n-Propyl-TCNQ	125—127	+0.10	−0.31	397 (6.0)	—	2
2,5-Dimethyl-TCNQ	265—267	+0.02	−0.28	403 (6.0)	—	2
11,11,12,12-Tetracyano-1,4-naphthoquinodimethane	244—245	−0.088	−0.36	288 (6.9) 392 (3.47) 409 (3.3)	1.49*	6
2-Diphenylmethyl-TCNQ	350—353	—	—	361 (2.56) 258 (0.665) 221 (1.77)	—	8

*Chatterjee's data[6].
**Farragher and Page's data[10].

TCNQ is a crystalline yellow-brown substance melting at 296—298°C and subliming readily above 250°C. In the solid state it is stable in air but in solutions it is sensitive to moisture[1]. According to X-ray diffraction data, the TCNQ unit cell has the following parameters: $a = 8.906$ Å, $b = 7.060$ Å, $c = 16.395$ Å, and $\beta = 98.54°$; its density is 1.315 g cm^{-3}. The bond lengths and angles in the TCNQ molecule are shown in Fig. 1. The distance between the planes of adjacent molecules in the crystal is 3.45 Å.[12]

The electronic spectrum of the acetonitrile solution of TCNQ shows one absorption band (395 nm, $\epsilon = 6.36 \times 10^4$)[1]; four maxima, at 304, 341, 402, and 424 nm, were found for the single crystal in polarised light along the a and b axes[13]. Quantum-chemical calculations on the TCNQ molecule[14-17] lead to a system of electronic transitions consistent both with the experimentally observed electronic absorption bands and with the photoelectronic spectra of TCNQ.[18,19]

The infrared[20-22] and Raman[23] spectra of TCNQ have been investigated in detail. The most intense infrared lines are at 3050 [ν(C—H)], 2220 [ν(C≡N)], 1540 [ν(C=C)], 1545 {ν[C=C(CN$_2$)]}, and 861 cm^{-1} [γ(C—H)] and in the Raman spectrum the most intense lines are at 3050 [ν(C—H)], 2225 [ν(C≡N)], 1602 {ν[C=C(CN)$_2$]}, 1554 [ν(C=C)], and 1210 [δ(C—H)].

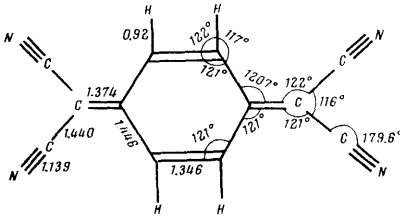


Figure 1.

According to ^{14}N nuclear quadrupole resonance data, the nitrogen atoms in the TCNQ molecule can occupy two non-equivalent positions. The average frequency of the quadrupole interaction constant is 4021 kHz for TCNQ. The observed asymmetry in the position of the nitrogen atoms can be explained by the non-equivalence of the polarisation of the π orbitals of the nitrile group parallel and at right angles to the plane of the ring[24].

According to its electrical properties, the TCNQ single crystal is a typical organic semiconductor (the conductivity at 20°C is 2×10^{-12} Ω^{-1} cm^{-1} and the activation energy for dark conduction is 0.6 eV [25-27]). Furthermore, TCNQ single crystals exhibit photoconduction[25,26]. Measurements of the electrical characteristics of TCNQ single crystals prepared in different ways showed that the single crystals, both grown *in vacuo* and obtained on cooling solutions, contain an admixture of the sodium salt of TCNQ owing to the leaching of glass; the dark conductivity is relatively insensitive to this impurity, while the photoconductivity depends strongly on its concentration[26].

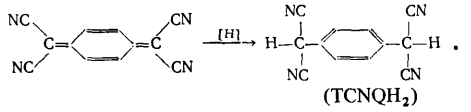
A special investigation of the influence of the admixture of the lithium salt of TCNQ on the electrical properties of TCNQ itself revealed the opposite effect of this additive: 1—2% of the salt impurity increased the dark current but hardly affected the photoconductivity[27]. This difference between the effects of impurities can probably be accounted for by their amount: whereas in the first instance we are probably dealing with 0.1—0.01%, in the second the concentration of the impurity is 1—2%.

III. CHEMICAL PROPERTIES

1. Addition Reactions

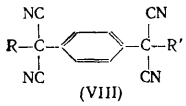
Whereas 1,4-addition reactions in which 3-substituted hydroquinones are formed are characteristic of p-benzoquinone, a structural analogue of TCNQ, 1,6-addition reactions are characteristic of TCNQ. The simplest example of such a reaction is the reduction of TCNQ by

thiophenol, mercaptoacetic acid, or hydriodic acid with formation of *p*-phenylenedimalononitrile ($TCNQH_2$): [1]



($TCNQH_2$)

TCNQ readily reacts with sulphur dioxide in aqueous acetonitrile to form the sulphonic acid (VIIIa). [1] In the absence of catalysts TCNQ does not react with halogens: in the reaction with chlorine in the presence of catalytic amounts of triethylamine or NMe_4Cl, the dichloro-derivative (VIIIb) was obtained:



(VIII)

(a) R=H, R′=SO_3H; (b) R=R′=Cl; (c) R=R′=Br; (d) R=R′=C(Me)$_2$CN; (e) R=H, R′=4-$C_6H_4NR''_2$; (f) R=H, R′=4-OH-2-R″C_6H_3; (g) R=H, R′-2-pyrrolyl; (h) R=H, R′=3-indolinyl; (i) R=H, R′-1-azulenyl; (j) R=HgOAc, R′=4-$C_6H_4NMe_2$.

The analogous bromo-derivative (VIIIc) is formed only when bromine interacts with the disodium salt of $TCNQH_2$.

The addition product (VIIId) was isolated in the thermal decomposition of $\alpha\alpha'$-azobisisobutyronitrile in the presence of TCNQ.

NN-Dimethylaniline also forms a 1,6-addition product (VIIIe, R″ = Me) with TCNQ. [1] A more detailed study of the interaction of TCNQ with a series of aromatic amines [28,29] showed that only the *para*-position relative to the amino-group is active in this reaction even in the case of amines such as *NN*-dimethyl-1-naphthylamine. A series of addition products (VIIIe) with R″ = H, Me, Et, Pr, Bu, or Ph were obtained. The only aromatic amines which react with TCNQ are those whose ionisation potential I_D is less than 7.8–8.0† eV or, what amounts to the same thing, amines which form complexes with TCNQ whose spectra contain a charge-transfer band above 600 nm (in chloroform).

TCNQ reacts with phenols very slowly to form compounds (VIIIf). The use of sodium phenoxide leads to an appreciable acceleration of the reaction [31]. This is apparently associated with the fact that the electron-donating properties of phenols are inadequate ($I_D > 8$ eV) and only phenoxide ions, the concentration of which is extremely low under the usual conditions (in acetonitrile), are involved in the reaction.

Pyrrole and indole react with TCNQ to form addition products (VIIIg) and (VIIIh) respectively. If the 2- and 5-positions in pyrrole are occupied, the 3- or 4-position is reactive. If the 3-position in indole is occupied, substitution takes place in the 2-position, but the reaction proceeds under more severe conditions [31].

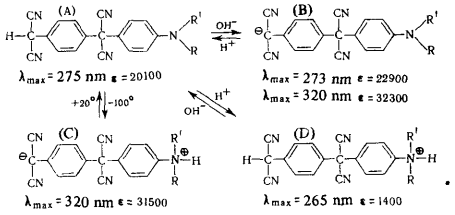
In acetonitrile TCNQ reacts readily with azulene; as in the case of TCNE, [32] this involves the formation of 1-substituted azulene derivatives (VIIIi). [33] An organomercury compound (VIIIj) was obtained by the reaction of TCNQ with *p*-*NN*-dimethylaminophenylmercury acetate [28].

It is noteworthy that, whereas the reactions involving the addition of chlorine and sulphur dioxide resemble nucleophilic reactions involving addition to the double bond and the addition of the dimethylacetonitrile radical resembles radical addition reactions, the interaction with aromatic amines, phenols, nitrogen-containing heterocycles, azulene, and *p*-dimethylaminophenylmercury acetate apparently begins with the addition of the electron donor to TCNQ with formation of the radical-ion TCNQ salt; the site where a hydrogen atom is substituted in the donor molecule is similar to that in electrophilic substitution under mild conditions [28]. The formation of $TCNQH_2$ in the reaction of TCNQ with triarylphosphine proceeds in accordance with this mechanism via the intermediate $TCNQ^{\cdot}$ radical-anion:

$$Ar_3P + TCNQ + H_2O \xrightarrow{H^+} Ar_3PO + TCNQH_2 .$$

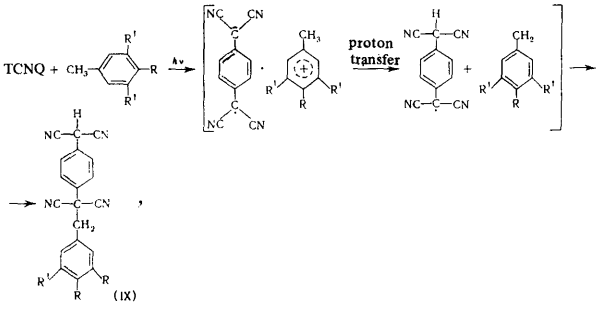
This was demonstrated in a kinetic study of the reaction using optically active arylphosphines [35].

The majority of compounds (VIII) contain the acid malononitrile hydrogen atom, which can be readily split off: as a result, these compounds are sensitive to the pH of the medium. This is particularly clearly seen for compounds (VIIIe), which can exist in four different forms in solution, differing in their electronic absorption spectra and capable of being reversibly converted into one another [reaction (5), compound (VIIIe), R = R′ = CH_3; (A) = undissociated compound, (B) = anion, (C) = inner salt, (D) = ammonium salt] [36]:



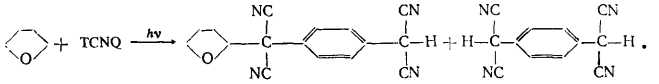
(5)

On illumination with light corresponding to the charge-transfer band of the TCNQ complexes with toluene, *p*-xylene, and mesitylene, compounds having the general formula (IX) are formed, probably via a stage involving the photoinduced addition of a proton to TCNQ: [37]



where R and R′ = H or Me.

Yet another example of radical addition to TCNQ is its interaction with tetrahydrofuran:



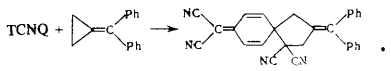
The reaction proceeds when a mixture of the initial compounds is illuminated by ultraviolet light or in the presence of peroxides [38].

In contrast to *p*-benzoquinone [39], TCNQ does not form Diels–Alder adducts with dienes: the reaction with cyclopentadiene and methylbuta-2,3-diene results in the formation of a polymeric product only [1].

An unusual reaction involving addition to TCNQ was discovered recently [40]. When TCNQ interacts with

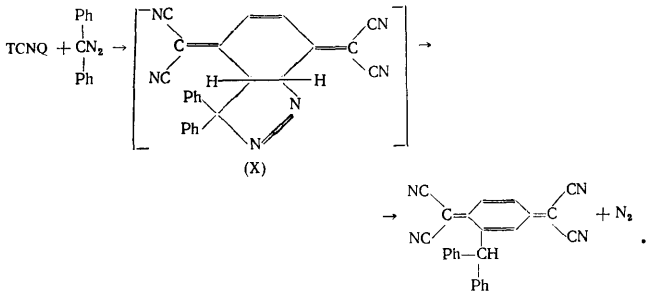
† The ionisation potential was determined by the photoionisation method; other methods give a somewhat higher value of I_D.

2,2-diphenylmethylenecyclopropane, the addition product with the structure shown below is formed in 60% yield:



2. Substitution Reactions

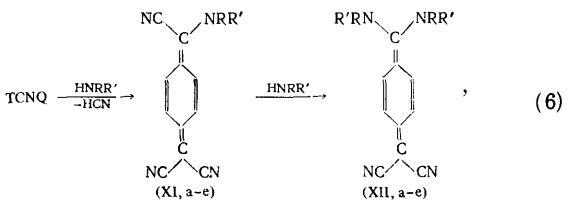
In principle two types of substitution reactions with TCNQ are possible: the substitution of hydrogen and of CN groups. The only example of reactions of the first type is the interaction of TCNQ with diphenyldiazomethane already mentioned [8]:



(X)

This involves the formation of 2-diphenylmethyl-TCNQ, probably via the intermediate cyclic derivative (X).

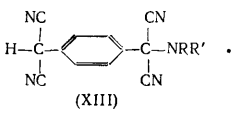
Among reactions of the second type, mention may be made of the interaction of TCNQ with primary and secondary aliphatic and aromatic amines [reaction (6)]: [41]



(XI, a-e) (XII, a-e) (6)

where R = R′ = H (a), R = H and R′ = Bu (b), NRR′ = *N*-pyrrolidinyl (c), R = H and R′ = 4-C_6H_4OMe (d), and R = H and R′ = NH_2 (e).

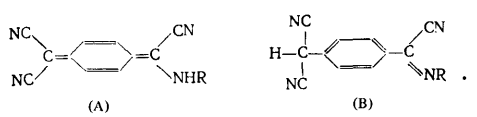
It is noteworthy that the reactions involving substitution of the cyano-groups in TCNQ apparently proceed via the formation of an intermediate product of 1,6-addition to the quinonoid system of TCNQ [compound (XIII)], which splits off HCN rapidly at room temperature and is converted into the corresponding compound (XI):



(XIII)

The spectra of intermediates of type (XIII) were observed for films, obtained by the simultaneous sputtering of TCNQ and electron donors (*p*-phenylenediamine or *m*-phenylenediamine) onto a support cooled to 77 K, when the film was heated slowly to room temperature [42].

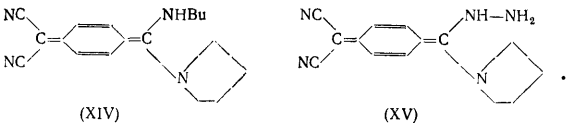
Aliphatic compounds (XI) [for example (XIb)] exist in the form of two isomers—(A) and (B): [41]



(A) (B)

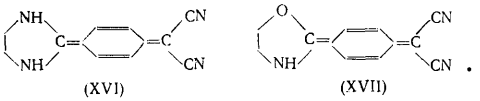
The *p*-anisidine derivative (XId) was obtained only in form (B). [41] Judging from the electronic spectra, *p*-phenylenediamine also gives rise to form (B), while *m*-phenylenediamine reacts with formation of the quinonoid form (A). [42]

Mixed derivatives of TCNQ have also been obtained by reaction with amines [compounds (XIV) and (XV)] [41]:



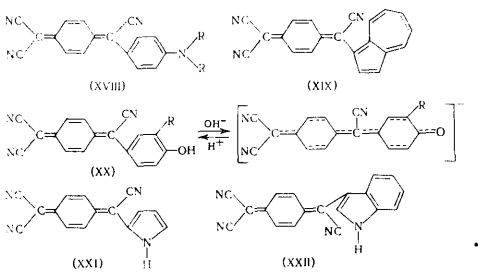
(XIV) (XV)

Bifunctional amines (for example, ethylenediamine and monoethanolamine) are capable of substituting two cyano-groups in TCNQ [compounds (XVI) and (XVII)] [41]:



(XVI) (XVII)

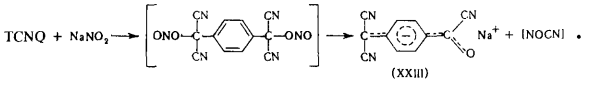
The products of the substitution of a cyano-group in TCNQ [compounds (XVIII)–(XXII)] have been obtained by ultraviolet irradiation of the corresponding products of the 1,6-addition reaction [compounds (VIII, e–i)]. They all have a deep colour (red for the product of the reaction with phenol and blue for all others); the position of their long-wavelength absorption band depends on the nature of the electron-donating group and varies from 500 to 700 nm. The absorption band itself is due to intramolecular charge-transfer [29,31,33]:



(XVIII) (XIX) (XX) (XXI) (XXII)

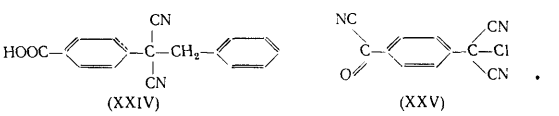
Compound (XX) contains an acid proton, which splits off reversibly in an alkaline medium to form an intensely blue anion [31].

Another example of substitution reactions of TCNQ is its interaction with sodium nitrite, which leads to the formation of an orange-red salt (XXIII) via a hypothetical intermediate addition product:



(XXIII)

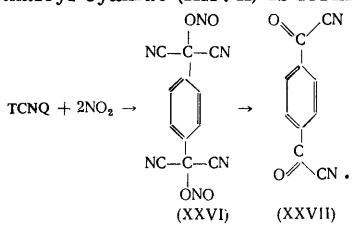
Like chlorination, benzylation of the salt (XXIII) (followed by hydrolysis) leads to the formation of the addition products (XXIV) and (XXV) respectively [41]:



(XXIV) (XXV)

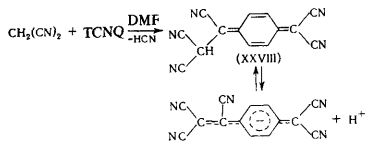
N_2O_4 reacts with TCNQ similarly to $NaNO_2$. When the reaction was carried out in acetonitrile at 0°C, an unstable intermediate, to which structure (XXVI) was attributed,

was obtained in 75% yield. On heating it *in vacuo* at 130°C, terephthaloyl cyanide (XXVII) is formed[41]:



(XXVI) (XXVII)

The substitution product (XXVIII) was obtained by the reaction of TCNQ with malononitrile in dimethylformamide (DMF):[43]



(XXVIII)

Compound (XXVIII) is a strong acid ($pK_a = 0.60$) and readily dissociates in solution to form an intensely blue carbanion; in strongly acid solutions, where the dissociation is suppressed, the colour of compound (XXVIII) differs little from that of TCNQ. Thus nucleophilic reactions involving 1,6-addition to the conjugated double bond system, which in many instances are the first stage of the CN substitution reactions, are most characteristic of TCNQ. The mechanism of these processes has been inadequately investigated, although it is of definite interest, since in some cases the reaction apparently proceeds via one-electron oxidation of the donor with formation of an intermediate radical-ion salt.

3. Complex Formation Reactions

The ability of quinones to form stable solid complexes with aromatic amines has been known for a long time[44]. TCNQ, a strong π acid, forms three types of complexes with electron-donating compounds[45]. Since these complexes are of much interest from the standpoint of their semiconducting properties, the dark conductivities σ are listed below as their characteristics. The first type includes classical molecular complexes in which mainly aromatic hydrocarbons are used as electron donors ($\sigma = 10^{-3}-10^{-14}\ \Omega^{-1}\ cm^{-1}$, Table 2).[45]

The second type of TCNQ complexes includes simple radical-ion salts having the general formula $M^{n+}(TCNQ^{\cdot-})_n$, where M^{n+} is a metal cation or organic cation with n charges, which represent the limiting case of molecular complexes: here the electron is completely transferred from the donor to the acceptor molecule ($\sigma = 10^{-4}-10^{-12}\ \Omega^{-1}\ cm^{-1}$).[45] We may note that such compounds are referred to in the literature as both strong complexes and as simple radical-ion salts. The electronic spectra of their solutions contain the absorption bands of the donor radical-cations and the $TCNQ^{\cdot-}$ radical-anion.

The third type of TCNQ complexes includes complex radical-ion salts having the general formula $M^+(TCNQ^{\cdot-}).(TCNQ^0)$, or $M^{2+}(TCNQ^{\cdot-})_2.(TCNQ^0)$. In solution these salts dissociate with formation of the donor cation, the $TCNQ^{\cdot-}$ radical-anion, and the neutral molecule $TCNQ^0$. However, in the crystal the electron is delocalised over both acceptor molecules and the radical-anion is of the form $(TCNQ^{\cdot-})_2$. As a rule these salts give rise to an intense ESR signal; their spin concentration may reach 1–1.5 spins per donor–acceptor pair. The complex radical-ion salts have a strikingly high conductivity[45]: $\sigma = 10^{-3}-10^{2}\ \Omega^{-1}\ cm^{-1}$.

It is noteworthy that there is no sharp boundary between weak molecular complexes and radical-ion salts. Thus the complex of TCNQ and *NNN'N'*-tetramethyl-*p*-phenylenediamine dissociates in acetonitrile with formation of a radical-ion pair[45].

Table 2. Molecular TCNQ complexes with aromatic donors[45].

Donor	Solvent used in synthesis	Yield, %	M.p., °C	Resistivity, Ω cm	λ_{max} of charge-transfer band, nm
NNN'N'-Tetramethyl-*p*-phenylenediamine	$CHCl_3$	71	128—129	10^6	1163[a]
NN-Dimethyl-*p*-phenylenediamine	$CHCl_3$	38	112—117	10^9	
Diaminodurene	THF	86	190 decomp.	10^9	
1,5-Diaminonaphthalene	$CHCl_3$	59	197 decomp.	10^9	
Anthracene	THF	42	282—283	10^{11}	845[b]
Pyrene	THF	52	260 decomp.	10^{12}	765[b]
Hydroquinone[c]	THF		180—185		
4,6,8-Trimethylazulene	THF	85	160—167	10^9	

[a] Kosower's data[46]. [b] Beukers and Szent-Gyorgyi's data[47]. [c] Molar ratio donor : TCNQ = 1 : 2.

A comparative study of the electronic spectra of a solution of this complex relative to those of the perchlorate of Wurster's Blue and the lithium salt of TCNQ showed that it is dissociated to an extent greater than 80%. The study of the polarisation absorption spectra of single crystals of the complex confirmed its partially ionic character[48]. Similar conclusions were reached also about the structure of TCNQ complexes with *NNN'N'*-tetramethylbenzidine and benzidine[49].

Table 3. TCNQ complexes forming clathrate compounds with solvents[50,51].

Donor	Solvent	Donor : acceptor : solvent molar ratio	Donor	Solvent	Donor : acceptor : solvent molar ratio
Benzidine	CH_2Cl_2	1,0:1,1:1,6	3,3'-Dichlorobenzidine	CH_2Cl_2	1,0:0,8:0,16
Benzidine	C_2H_5Br	1,0:1,1:1,6			
Benzidine	MeCOMe	1,0:0,8:0,8	*o*-Toluidine	CH_2Cl_2	1,0:1,0:0,23
3,3'-Diaminobenzidine	CH_2Cl_2	1,0:1,0:0,45	*o*-Toluidine	$CHCl_3$	1,00:1,07:0,52

It was found that certain solvents form clathrate compounds with TCNQ complexes (Table 3)[50,51]. Their crystal structures[52] and electrical properties[53] have been investigated.

The ability of TCNQ to undergo readily one-electron reduction under the influence of certain metals, metal iodides, or the iodides of organic cations has been used to synthesise simple TCNQ radical-ion salts[45]. Thus copper or silver readily react with TCNQ in acetone or acetonitrile at room temperature:

$$Cu + TCNQ \rightarrow Cu^+TCNQ^{\cdot-},$$

$$Ag + TCNQ \rightarrow Ag^+TCNQ^{\cdot-},$$

$$MI + TCNQ \rightarrow M^+TCNQ^{\cdot-} + \frac{1}{2}I_2,$$

where M is the metal or organic cation.

It has been shown that the TCNQ + $I^- \rightleftharpoons TCNQ^{\cdot-} + \frac{1}{2}I_2$ system is reversible. The standard reduction potential of TCNQ is 0.581 V relative to the standard hydrogen electrode[54].

There are several ways of synthesising simple radical-ion TCNQ salts[45]. The first procedure (*a*) involves the interaction of metal iodides with TCNQ. TCNQ salts with lithium, sodium, potassium, copper, etc. have been obtained in this way. The maximum yield of the salt is reached when the reactant ratio corresponds to the equation

$$3LiI + 2\ TCNQ \rightarrow 2Li^+TCNQ^{\cdot-} + Li^+ + I_3^- .$$

In the second method (*b*) TCNQ radical-ion salts are obtained by the exchange reaction between the lithium salt of TCNQ, which is readily soluble in water or acetonitrile, with a soluble metal salt or the salt of an organic cation. Examples of the syntheses of certain salts by this procedure[47] are presented below:

$$Li^+\ TCNQ^{\cdot-} + FeSO_4 \xrightarrow{H_2O} Fe^{++}(\ TCNQ^{\cdot-})_2 \cdot 3H_2O ,$$
$$Li^+\ TCNQ^{\cdot-} + AgNO_3 \xrightarrow{H_2O} Ag^+\ TCNQ^{\cdot-} , \qquad (7)$$
$$Li^+\ TCNQ^{\cdot-} + Et_3NH^+I^- \xrightarrow{CH_3CN} Et_3NH^+\ TCNQ^{\cdot-} ,$$

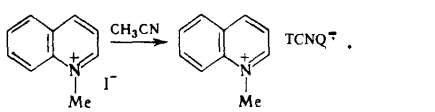


Table 4. The constants and methods of synthesis of simple TCNQ salts.

Cation	Method of synthesis	Solvent	Yield, %	Decomp., temp., °C	Resistivity, Ω cm
Li^+	(*a*)	CH_3CN	98	>300	$2\cdot10^5$
Na^+	(*a*)	CH_3CN	59	>300	$3\cdot10^4$
K^+	(*a*)	CH_3CN	70	>300	$5\cdot10^3$
Cs^+	(*b*)	CH_3CN	67	—	$3\cdot10^4$
Ba^{++}	(*a*)	CH_3CN	70	—	$8\cdot10^5$
Cu^+	(*a*)	CH_3CN	54	—	$2\cdot10^2$
Cu^{++}	(*b*)	CH_3CN	80	—	$2\cdot10^2$
$Cu(NH_3)_2^{++}$	(*b*)	CH_3CN	94	—	$7\cdot10^2$
NH_4^+	(*a*)	THF–MeOH	60	210—215	$6\cdot10^4$
Et_3NH^+	(*b*)	H_2O	81	~180	10^9
$(n\text{-}Bu)_4N^+$	(*b*)	H_2O	—	135	10^{12}
Morpholinium	(*a*)	CH_3CN	35	~220	10^9
$Ph_3(Me)P^+$	(*b*)	H_2O	99	~170	$4\cdot10^{10}$
Pyridinium	(*c*)	CH_3CN	59	158—195	10^8
N-Methylpyridinium	(*b*)	CH_3CN—EtOH	—	~235	10^5
N-Methylquinolinium	(*b*)	CH_3CN—EtOH	76	240—244	10^7
5,8-Dihydroxyquinolinium	(*d*)	$CHCl_3$	72	168—169	15

The third method (*c*), the interaction of an amine with $TCNQH_2$ and with TCNQ, has been considered in detail in connection with the synthesis of complex TCNQ salts [see reaction (9)] and the fourth method (*d*) involves the direct interaction of an amine with TCNQ. Table 4 presents data concerning the method of synthesis and certain characteristics of a number of simple TCNQ salts[45].

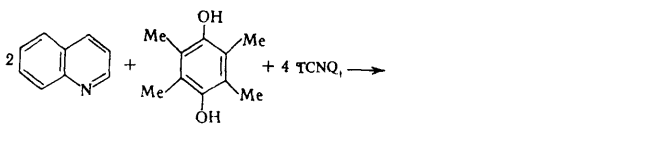
The methods of synthesis of complex TCNQ radical-ion salts are illustrated by Eqn. (8) for the synthesis of a complex triethylammonium radical-ion salt (XXIX) (the yield of the salt is indicated in brackets)[45]:

$$\text{(a)}\ Et_3NH^+\ TCNQ^{\cdot-} + TCNQ \rightarrow Et_3NH^+(\ TCNQ)_2^{\cdot-}\ (XXIX)\ \ (50\%) ,$$
$$\text{(b)}\ 3Et_3NH^+I^- + 2TCNQ \rightarrow (XXIX)\ \ (50\%) , \qquad (8)$$
$$\text{(c)}\ 2Et_3N + TCNQH_2 + 3TCNQ \rightarrow (XXIX)\ \ (90\%) ,$$
$$\text{(d)}\ Et_3N + 2TCNQ \rightarrow (XXIX)\ \ (77\%) .$$

In the first method (*a*) one mixes hot solutions of a simple TCNQ salt and neutral TCNQ; the complex TCNQ salt crystallises on cooling. This method is used when the complex salt is much less soluble in the given solvent than the simple salt.

In the second method (*b*) the complex salt is obtained from TCNQ and a metal iodide or the iodide of an organic cation, the iodide ion reducing TCNQ.

In the synthesis of complex TCNQ salts by the third method (*c*), the starting materials are TCNQ and $TCNQH_2$ [reaction (9)]:



(9)

In one of the versions of this method (*b'*) durohydroquinone is used as the proton and electron donor:

Table 5. The constants and methods of synthesis of certain complex TCNQ salts.

Cation	Method of synthesis	Solvent	Yield, %	Decomp. temp., °C	Resistivity, Ω cm
$(Et)_3NH^+$	(*d*)	THF	77	>195	20
	(*a*)	CH_3CN	32	—	—
	(*c*)	CH_3CN	62	—	—
$(Me)_3NH^+$	(*d*)	THF	90	>215	$5\cdot10^6$
$(Et)_4N^+$	(*a*)	CH_3CN	79	255—268	$2\cdot10^4$
Cs^+ *	(*a*)	CH_3CN	82	—	$9\cdot10^4$
Morpholinium*	(*a*)	CH_3CN	40	210	10^5
Pyridinium	(*c*)	CH_3CN	42	168—185	37
Quinolinium	(*b*)	CH_3CN	91	~250	0.5
	(*b*)	CH_2Cl_2	44	—	—
	(*c*)	CH_3CN	87	—	—
	(*c'*)	CH_3CN	71	—	—
N-Methylquinolinium	(*a*)	CH_3CN	22	245—250	3
N-Ethylquinolinium	(*a*)	CH_3CN	—	237—239	8
Ferricinium	(*d*)	CH_3CN	—	—	0,24
$Ph_3(Me)P^+$	(*a*)	CH_3CN	60	231—233	60; 600; 10^5**
Ph_4P^+	(*a*)	CH_3CN	33	228—237	10^3; 10^6; $2\cdot10^6$**
$Ph_3(Me)As^+$	(*a*)	CH_3CN	56	224—227	57; 900; 10^5**
Ph_4Sb^+	(*a*)	CH_3CN	42	219—220	13; 1.5; 10^4; **

*The composition of the complex was $(cation^+)_2.(TCNQ^{\cdot-})_2$. .TCNQ, while in the remaining cases the composition was $(cation^+).(TCNQ^{\cdot-}).TCNQ$.

**The resistivities of single crystals in three crystallographic directions are quoted.

The fourth method (*d*) is used to synthesise complex salts of TCNQ and aliphatic amines. The solvent apparently serves as the proton donor in this case, although the reaction mechanism has not been elucidated[45]. Data concerning the synthesis and properties of complex TCNQ radical-ion salts are presented in Table 5.

New methods for the synthesis of TCNQ salts have been described recently. Thus thin polycrystalline films of alkali metal (M) salts of TCNQ having the 1 : 1 (M = Li, Na, K, or Rb) and 2 : 3 (M = Cs) compositions were obtained by the successive vacuum sputtering of the metal and TCNQ.[54]

The interaction of TCNQ with distannane leads to the oxidation of the latter and the formation of a radical-ion salt[55]:

$$R_3Sn{-}SnR_3 + 2TCNQ \xrightarrow{THF} 2\,(R_3Sn)^+\,(TCNQ)^-,$$

where R = Me or Bu.

Although the following reaction can hardly be regarded as a method for the synthesis of the radical-ion salts, it too leads to the formation of a salt[56]:

$$2Ph{-}C{\equiv}CCu + 2TCNQ \rightarrow 2Cu^+\,(TCNQ)^- + Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph\ .$$

There is an extensive literature on the synthesis of TCNQ complexes and salts, but we shall consider only reports of studies which in our opinion are of greatest interest and which make it possible to illustrate the wide variety of electron-donating compounds employed.

TCNQ complexes with aminoazo-dyes have been investigated[57]. Numerous simple and complex TCNQ salts with cationic dyes (primarily cyanine dyes) have been studied[58-60] and simple and complex TCNQ salts with *N*-methylpyrazine and its benzo-derivatives[61], with hydroxy- and halogeno-derivatives of piperidine and pyrrolidine[62], and with polyepichlorohydrin[63] have been synthesised. Simple and complex TCNQ salts with arenechromium compounds (for example with dibenzenechromium) have been obtained[64] and numerous TCNQ complexes with *p*-aminobenzenesulphonamide and its derivatives have been investigated[65]. TCNQ radical-ion salts with cobalt complexes[66], platinum, palladium, and nickel complexes[67], and copper, iron, and nickel chelates[68] have been synthesised.

Ternary (1 : 1 : 1) TCNQ complexes with dyes containing the molecule of a second acceptor [iodine[69] and 9-dicyanomethylene-2,4,7-trinitrofluorenone (XXX)] have been investigated[70]. The latter complex dissociates in solution into the dye cation, the TCNQ anion, and the neutral molecule of compound (XXX). The structure of this complex consists of a collection of parallel stacks of the donor and the acceptor, the TCNQ and (XXXX) molecules alternating in the acceptor stack[71].

IV. PHYSICOCHEMICAL PROPERTIES OF 7,7,8,8-TETRACYANOQUINODIMETHANE COMPLEXES

1. Crystal Structure

Both the optical and electrical properties of TCNQ complexes depend directly on their crystal structure and for this reason we shall consider initially the structures of solid TCNQ complexes. Since data on the structures of the complexes have been recently surveyed in a review[72], we shall only briefly enumerate the principal characteristics of the structures of TCNQ complexes, including the results of studies in recent years.

Molecular TCNQ complexes have a structure which differs sharply from that of the radical-ion salts. Like complexes containing other well-known electron acceptors, they consist of infinite stacks in which donor and acceptor molecules alternate. The molecular planes of the donor and acceptor are approximately parallel and the distances between them (3.4–3.7 Å) are typical for weak intermolecular bonds (Table 6). The bond lengths and the valence angles in the molecules hardly change under these conditions. It has recently been found[76] that there is a direct proportionality between the donor–acceptor distance in TCNQ molecular complexes and the difference between the ionisation potential of the donor and the electron affinity of the acceptor (after Briegleb[82]).

Table 6. The donor–acceptor distances in TCNQ complexes.

Donor	Donor–acceptor distance, Å	References
Hexamethylbenzene	3.65	72
Anthracene	3.50	72
Acenaphthene	3.35	73
Pyrene	3.50	74
Perylene	3.44	75
Phenazine	3.38	76
Phenothiazine	3.52	77
1,10-Phenanthroline	3.45	78
Dibenzo-*p*-dioxin	3.46	79
N-Methylphenothiazine	3.44	72
Bis-(8-hydroxyquinolinato)copper(II)	3.2	72
NNN'N'-Tetramethyl-*p*-phenylenediamine	3.27	72
Carbazole*	3.44	80
NN-Dimethyldihydrophenazine**	3.22	81

*The crystal consists of domains in each of which the donor molecules are oriented in the same way[80].
**In the stack the donor and acceptor form a pair with an interplanar distance of 3.22 Å; the distance between the pairs is 3.54 Å.

The TCNQ–benzidine complex and its clathrate compounds with solvents consist of infinite stacks of alternating donor and acceptor molecules forming structures of three types. The first type, a complex without the solvent[83], consists of uniform stacks with an interplanar distance of 3.22 Å. The complex containing dichloromethane is made up to stacks in which the distance between the donor and acceptor is the same (3.22 Å) and the solvent molecules are accommodated in the channels between the stacks[84]. Complexes containing acetonitrile, acetone, and methylene chloride are constructed in exactly the same way. A third type of structure has been demonstrated for the complex containing benzene[85]. In this case the stacks consist of donor and acceptor dimers with an interplanar distance of 3.09 Å, benzene molecules being distributed in the channels between the stacks. Complexes containing toluene, nitrobenzene, and benzonitrile have similar structures.

TCNQ radical-ion salts are constructed differently. Since there are no fundamental differences between the structures of simple and complex TCNQ salts, we shall consider their structures by arranging the salts in groups based on different types of packing of anions.

Both simple and complex TCNQ salts consist in most cases of individual infinite stacks of anions. If the donor molecules are fairly planar, they can also form an infinite stack parallel to that of the acceptor. For spherical cations (for example, metal and ammonium cations), the donors are arranged in separate structures consisting of chains between the stacks of anions and parallel to the latter. Data for the structures of the TCNQ salts are

compiled in Table 7, in which the crystalline modification of the salt, the type of packing of the anions, the distance between neighbouring acceptor molecules, and the resistivity of the salt are indicated. The resistivity of TCNQ salt single crystals is minimal in the direction of the stack of anions and the anisotropy of the conductivity as a function of direction in the crystal can reach 10^4 (Table 6), so that the resistivity of the salt depends on the way in which the stack of anions is constructed.

The first group of salts have the highest resistivities (Table 7, compounds 1–5). The study of the structures of these salts showed that they do not contain stacks of anions at all, individual pairs or tetrads of anions separated by cations being present.

Table 7. The crystal structures of TCNQ radical-ion salts.

No.	Cation(donor)	Crystalline modification	Donor: acceptor	Structural formations	Distance between TCQD species, A	Refs.	Resistivity, Ω cm	Refs.
1	1,3-Dimethylbenzimidazole	Triclinic	1:1	Dimers	3.07	86	1.5×10^7	87
2	1,2,3-Trimethylbenzimidazole	Monoclinic	1:1	Dimers	3.12	88	1.4×10^9	87
3	3,3'-Diethylthiacyanine	Triclinic	1:1	Dimers	3.23	72	9×10^9	72
4	Dibenzenechromium	Monoclinic	1:1	Dimers	3.28	72	1.6×10^7	72
5	1,3,3'-Trimethyl-2-[*p*-(*N*-β-chloroethyl-*N*-methylamino)-styryl]indole	Monoclinic	1:2	Tetrads	w.t.[a]3.22 b.t.[b]3.45	72	–	–
6	Na	Triclinic	1:1	Stacks, two types of dimers	w.d.[c]3.22 w.d.[d]3.20 b.d.3.50 b.d.3.48	89	3×10^4	45
7	Rb-I (T = –190°C)	Monoclinic	1:1	Stacks, dimers	w.d.3.16	90	1×10^5	91
8	Ditoluenechromium	Monoclinic	1:1	Stacks, dimers	w.d.3.33 b.d.3.42	72	2.5×10^5	72
9	Morpholinium	Triclinic	1:1	Stacks, dimers	w.d.3.28 b.d.3.61	92	1×10^2	45
10	3,3'-Dimethylthiocyanine	Monoclinic	1:2	Stacks, dimers	w.d.3.25 b.d.3.38	93	2.3×10^3	93
11	3,3'-Dimethylthiocarbocyanine	Monoclinic	1:2	Stacks, dimers	w.d.3.17 b.d.3.17	94	4.6×10^5	94
12	3,3'-Diethylthiocarbocyanine	Monoclinic	1:2	Stacks, dimers	w.d.3.24 b.d.3.24	95	6.6×10^3	95
		Triclinic	1:2	Tetrads	3.28	96	5×10^4	95
13	1,1'-Ethylene-2,2'-bipyridylium	Triclinic	1:2	Stacks, two types of dimers	w.d.3.22 w.d.3.26 b.d.3.59	97	1×10^3	97
14	*NN*-Dibenzyl-4,4'-bipyridylium	Triclinic	1:4	Stacks, tetrads	w.d.3.16 b.d.3.24 b.t.3.62	98	–	–
15	Triethylammonium	Triclinic	1:2	Stacks, dimers	w.d.3.22 b.d.3.30	99	0.3[e] 35; 7.2×10^2	99
16	Tetraphenylphosphonium	Monoclinic	1:2	Stacks, two types of dimers	w.d.3.12 w.d.3.21 b.d.3.35 b.d.3.49	72	4.5×10^3 1.7×10^6 2.1×10^6	72
17	Methyltriphenylarsonium	Triclinic	1:2	Stacks, tetrads	w.t.3.20 b.t.3.58	72	5.7×10^3 9×10^2 1×10^5	45
18	Methyltriphenylphosphonium ($T < 40$°C)	Triclinic	1:2	Stacks, tetrads	w.d.3.22 b.d.3.24 b.t.3.57	72	6×10^1 6×10^2 1×10^5	45
	$T > 40$°C	Triclinic	1:2	Stacks, tetrads	w.d.3.26 b.d.3.32 b.t.3.55	100	–	–
19	*N*-Propylquinolinium	Triclinic	1:2	Stacks, tetrads	w.d.3.24 b.d.3.28 b.t.3.43	101	0.5 6 4.5×10^2	45
20	3-Ethyl-1-methylbenzimidazolium	Triclinic	1:2	Stacks, two pairs of dimers	w.d.3.28 w.d.3.27 b.d.3.32	102	0.15 2.3×10^2 4.3×10^2	102
21	3-Ethyl-1,2-dimethylbenzimidazolium	Triclinic	1:2	Stacks, two pairs of dimers	w.d.3.21 w.d.3.27 b.d.3.38	103	15	103
22	Cs	Orthorhombic	2:3	Stacks, triads	w.t.3.22 b.t.3.26	72	1×10^3	72
23	Morpholinium	Monoclinic	2:3	Stacks, triads	w.t.3.25 b.t.3.24	104	5×10^3	45
24	Trimethylammonium	Monoclinic	2:3	Stacks, triads	w.t.3.26 b.t.5.15	105	–	–
25	K	Monoclinic	1:1	Stacks	3.40–3.50	72	1×10^4	45
26	Rb-II (T = 20°C)	Triclinic	1:1	Stacks	3.43	91	1×10^2	91
27	Ditoluenechromium	Triclinic	1:1	Stacks	3.29	72	0.5	72
28	*NNN'N'*-Tetramethyl-*p*-phenylenediamine	Triclinic	1:2	Stacks	3.24	72	–	–

[a] w.t. = within triad or tetrad. [b] b.t. = between triads or tetrads. [c] w.d. = within dimer. [d] b.d. = between dimers. [e] The resistivities of single crystals in three crystallographic directions are quoted.

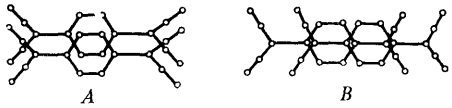


Figure 2.

The second most numerous group of salts (Table 7, compounds 6–24) contains inhomogeneous stacks of anions consisting of dimers, triads, or tetrads comprising the acceptor. The arrangement of neighbouring anions in the dimers is illustrated in Fig. 2*a*. In this arrangement the overlapping of the π orbitals of neighbouring molecules is optimal and in the majority of salts the arrangement of neighbouring anions in the dimers is of this type or similar. Examples of the arrangement of the anions in the stack between adjacent dimers are illustrated in Fig. 2*b*. The molecules are displaced along the long or short molecular axis relative to the optimal arrangement, which leads to an increase of the interplanar distance between neighbouring anions and this in turn leads to the variation of the resistivities of these salts from 10^5 to 1 Ω cm. In some cases, although the distance between the dimers is the same as that between the anions within the dimers (Table 7, compounds 11 and 12), the TCNQ molecules are displaced even more markedly than shown in Fig. 2*b* and there is almost no interaction between the dimers.

When the anions are grouped into tetrads, the latter usually consist of two dimers with optimal overlapping of the anions; the overlapping between pairs is as a rule intermediate between types (*a*) and (*b*) and that between tetrads is of type (*b*) or similar. There also exist tetrads in which the anions are distributed at the same distance, for example in the methyltriphenylarsonium salt of TCNQ.

It is noteworthy that formally complex salts should contain neutral TCNQ molecules. The study of the crystal structures of the salts and also comparison of the bond lengths and angles in the acceptor molecule showed that the charge in the complex salts is as a rule uniformly distributed between TCNQ and $TCNQ^0$, but this does not lead to the appearance of any new structural features in such salts. 2 : 3 Salts (Table 7, compounds 22–24), which have been combined into the second group, constitute an exception. Triads, in which the central acceptor molecule is neutral and two anions are present on either side of this molecule at the same distances have been detected in the structure of these salts. Since in many cases the accuracy of the determination of this structure is low, it is difficult to establish whether the stack contains neutral TCNQ molecules or whether the charge is distributed uniformly among all the acceptor molecules, so that this subgroup of salts may be much more extensive.

Uniform stacks of anions are characteristic of the third group of salts (Table 7, compounds 25–28); here the resistivity of the salt decreases with decrease of the distance between the anions. The third group includes also the structure of TCNQ salts, which exhibit a "metallic" temperature variation of the conductivity (the conductivity increases with decrease of temperature). In all these salts there is phase transition at a certain temperature and they are converted from an "organic one-dimensional metal" into a dielectric. Table 8 presents data for the structures of these salts, their conductivities, and their phase transition temperatures. Very short interplanar spacings in the stacks of anions and cations and correspondingly the highest conductivity known for organic compounds are characteristic of these salts.

Table 8. The crystal structures of TCNQ radical-ion salts with metallic type of conductivity.

Donor (cation)	Donor: acceptor	Distance between neighbouring species in stack		T_{trans}, K	$\sigma_{300\,K}$, Ω^{-1} cm^{-1}	References
		anions	cations			
Tetraselenofulvalene	1:1	*	*	40	800	106
Tetrathiofulvalene	1:1	3.17	3.47	58	600	107
Tetrathiotetracene	1:2	3.18	3.52	90	20—160	108
N-Methylphenazinium	1:1	3.26	3.36	200	140	109
Quinolinium	1:2	3.22	3.50	240	100	109
Acridinium	1:2	3.25	3.42	150	—	109

*According to preliminary data [106], the structure of the TSF–TCNQ complex is very close to that of the TTF–TCNQ complex.

Salts with infinite stacks of anions, each of which contains a free electron, may be regarded as quasi-one-dimensional metals; we shall return to the properties of these systems in discussing the electrical and magnetic properties of TCNQ complexes.

2. Spectroscopic Properties

As mentioned above, the electronic absorption spectra of TCNQ molecular complexes contain, apart from the absorption bands of the donor and acceptor, also a charge-transfer band (TCB). The appearance of the latter is a characteristic feature of the formation of complexes and spectroscopic evidence for the formation of complexes with TCNQ is frequently used [67,110–113]. Table 9 indicates the positions of the charge-transfer bands for a number of TCNQ molecular complexes with various aromatic donors. Evidently the position of this band can vary within very wide limits.

With increase of the strength of the donor (with decrease of its ionisation potential), TCNQ complexes become increasingly more ionic and in the case of a radical-ion salt an overall spectrum of the donor and acceptor ions is observed. The spectra of complexes of intermediate strength [stability?] contain bands due to the donor cation and the $TCNQ^-$ anion in addition to those of the donor and acceptor and the charge-transfer band. This was clearly demonstrated in a study of the electronic absorption spectra of complexes of a single donor with a series of acceptors. Thus,1,6-diaminopyrene forms molecular complexes with chloranil, bromanil, and iodanil, while TCNQ gives rise to radical-ion salts [118]. Similar results were obtained for a series of complexes of poly-(*p*-dimethylaminostyrene) [119].

Table 9. The positions of the charge-transfer band in the spectra of TCNQ complexes.

Donor	λ_{max}, nm	Solvent*	Refs.	Donor	λ_{max}, nm	Solvent*	Refs.
Hexamethylbenzene	595	A	47	*NN*-Di-n-butylaniline	940	A	28
Pentamethylbenzene	540	B	113	*p*-Toluidine	820	C	116
Biphenyl	510	A	47	*NN*-Dimethyl-*p*-toluidine	830	A	28
trans-Stilbene	635	A	47	4-Bromo-*NN*-dimethylaniline	755	A	28
Naphthalene	588	A	47	Diphenylamine	885	C	116
Anthracene	823	A	47	Triphenylamine	960	C	116
Phenanthrene	535	A	114	1-Naphthylamine	788	A	47
Pyrene	763	A	47	*NN*-Dimethyl-1-naphthylamine	800	A	28
Naphthacene	1040	A	47	*NN*-Dimethyl-2-naphthylamine	820	A	28
1,2-Benzopyrene	610	B	112	Indole	625	A	47
3,4-Benzopyrene	862	A	47	Catechol	540	A	47
Perylene	950	A	47	Anisole	530	A	28
3-Methylchloranthrene	925	A	47	Phenetole	545	A	28
Fluorene	607	B	114	Veratrol	583	A	28
Phenoxazine	820	A	115	2-Naphthol	653	A	47
Phenoxazine	1160	A	115	4-Aminoazobenzene	740	A	56
Phenothiazine	1200	A	115	4-Dimethylaminoazobenzene	950	A	56
N-Methylphenothiazine	1250	A	115	4-Dimethylamino-4'-methylthioazobenzene	970	A	56
1,2-Benzofluorene	635	B	116	4-Diethylaminoazobenzene	875	A	56
Carbazole	578	B	114	4-Ethyl-4'-diethylaminoazobenzene	1000	A	56
Thiophen	480	A	28	*p*-Phenylenediamine	628	C	116
Dibenzothiophen	526	B	114		875		
Dibenzofuran	510	B	114	*m*-Phenylenediamine	840	C	116
Chrysene	628	B	47	*NNN'N'*-Tetramethyl-*p*-phenylenediamine	620	C	116
					1055		
Coronene	740	A	47		1163	B	117
Triphenylene	575	A	47	2,3,5,6-Tetramethyl-*p*-phenylenediamine	630	C	116
					875		
p-Terphenyl	598	A	47	Benzidine	535	C	116
					1020		
Aniline	736	C	116	*NNN'N'*-Tetramethylbenzidine	550	C	116
					1285		
N-Methylaniline	752	A	47	Di-(4-aminophenyl)amine	610	C	116
N-Ethylaniline	758	A	47		875		
Acetanilide	550	A	28		1110		
N-Methylacetanilide	590	A	28				
NN-Dimethylaniline	835	C	116				
NN-Diethylaniline	880	A	–				
NN-Di-n-propylaniline	920	A	28				

*A = chloroform, B = methylene chloride, and C = polycrystalline film.

A very large number of studies have been made on the spectra of TCNQ radical-ion salts. It was established initially that the $TCNQ^-$ radical-anion in acetonitrile solution has a fairly complex spectrum, consisting of two main bands with λ_{max} = 420 nm (ϵ = 24 300) and 842 nm (ϵ = 43 300) and several weak bands with λ_{max} = 665, 680, 744, and 760 nm. [45] It follows from these results that the intensity ratio of the bands with λ_{max} = 420 and 842 nm for simple TCNQ radical-ion salts is 0.5, which is one of the main characteristics of simple TCNQ salts. For comparison, one may point out that the absorption spectrum of the 11,11,12,12-tetracyano-2,6-naphthoquinodimethane radical-anion has bands with λ_{max} = 1105 nm (ϵ = 66 200), 938 nm (ϵ = 23 500), 838 nm (ϵ = 5800), 518 nm (ϵ = 12 600), and 418 nm (ϵ = 25 500). [2]

In aqueous solutions the $TCNQ^-$ radical-anion forms dimers, which has been established in a spectrophotometric study of solutions of the lithium salt of TCNQ in water.

In other solvents (methylformamide, methanol, acetonitrile) dimerisation was not observed. The dimer has an absorption band with $\lambda max = 643$ nm.[120] The equilibrium constant for the dimerisation reaction $2\,TCNQ^- \rightleftharpoons (TCNQ)_2^{2-}$ proved to be 1.2×10^4 litre mole^{-1} at 14°C.[121]

Table 10. The parameters of the reflection spectra of simple (Nos. 1–16) and complex (Nos. 17–24) TCNQ radical-ion salts.

No.	Salt	λ_{max} for different bands, nm			Refs.
		α	β	CTB	
1	Li^+-$TCNQ^-$	364	617	1280	122
2	Na^+-$TCNQ^-$	364	613	1075	122
3	K^+-$TCNQ^-$	360	610	1180	122
4	NH_4^+-$TCNQ^-$	376	655	970	122
5	$Ph_3(Me)P^+$-$TCNQ^-$	375	655	970	122
6	Rb^+-$TCNQ^-$-I	369	635	1030	123
7	Ni^{2+}-$(TCNQ^-)_2$	395; 375	635	1110	123
8	Fe^{2+}-$(TCNQ^-)_2$	392; 372	650	1165; 950	123
9	Co^{2+}-$(TCNQ^-)_2$	400; 376	650	1135; 950	123
10	Mn^{2+}-$(TCNQ^-)_2$	400; 388	655	1110	123
11	Rb^+-$TCNQ^-$-II	356	600	1350	123
12	Cs^+-$TCNQ^-$	364	715; 625	1390;1075	123
13	Ba^{2+}-$(TCNQ^-)_2$	382	725; 650	1000	123
14	Morpholinium$^+$-$TCNQ^-$	362	615	1050	122
15	*N*-Methylphenazinium$^+$-$TCNQ^-$	388	620	850	122
16	*N*-Methylquinolinium$^+$-$TCNQ^-$	395	675		122
17	Cs_2^+-$(TCNQ)_3^{2-}$	364	617	990	131
18	(Morpholinium$^+$)$_2$-$(TCNQ)_3^{2-}$	364	614	1000	131
19	$Ph_3(Me)P^+$-$(TCNQ)_2^-$	380	585	962; 877	131
20	$Me_3(Ph)N^+$-$(TCNQ)_2^-$	380	610	980; 870	131
21	Et_3NH^+-$(TCNQ)_2^-$	368	610	972; 887	131
22	Quinolinium$^+$-$(TCNQ)_2^-$	375	575	953	131
23	*N*-Methylacridinium$^+$-$(TCNQ)_2^-$	364	562	895	131
24	*N*-Methylquinolinium$^+$-$(TCNQ)_2^-$	375	575	887; 980	131

The study of the reflection spectra of crystalline simple radical-ion TCNQ salts showed that they differ appreciably from those of the solutions. The reflection spectrum contains three types of lines, designated as the α, β, and charge-transfer lines. Data for some complexes are presented in Table 10 (compounds 1–16). Some investigators regard the α and β bands as the absorption bands of the monomeric TCNQ anions[124,125] which have been strongly displaced relative to their positions in the spectrum of the solutions (420 and 842 nm in acetonitrile), while others regard them as the absorption bands of $TCNQ^-$ dimers (380 and 647 nm in water)[120–130]. The charge-transfer band has been assigned to charge transfer between $TCNQ^-$ anions.

A more thorough recent study of the reflection spectra of simple TCNQ salts and comparison of the spectra with the crystal structure of the salts make it possible to divide the salts into three groups[123]. For the first group of salts, the α and β bands are probably those of the dimers (Table 10, compounds 1–10). The second group occupies an intermediate position. For the third group, the α and β bands are more likely to be those of monomeric $TCNQ^-$ anions which have been strongly displaced (compounds 13 and 14). Although new data for the structure of TCNQ salts (for example Refs. 89–92) throw doubt on the validity of the assignment of the individual salts to a particular group, the overall approach appears to be extremely promising for the elucidation of the dependence of the spectroscopic properties of TCNQ salts on their structure and also for the investigation of the nature of the interaction between the anions in the columns.

The study of the reflection spectra of complex crystalline TCNQ salts showed that they too contain three types of bands (Table 10, compounds 17–24)[131]. Those of highly conducting complex salts show only one explicit electronic absorption band in the range 2000–3500 nm. It has been suggested that this is a band corresponding to charge transfer between neutral TCNQ and its radical-anion[129].

The study of the mirror reflection spectra of single crystals of two complex TCNQ salts with triethylamine and 3,3′-diethylthiocarbocyanine in polarised light showed that the charge-transfer band as well as a band at longer wavelengths are polarised in the direction of the chains of $TCNQ^-$ anions and are due to electron transfer between two $TCNQ^-$ radical-anions (the first band)[127] and between a radical-anion and a neutral TCNQ molecule (the second band)[127].

A bathochromic shift of the α and β bands was observed in a study of the electronic spectra of the lithium and potassium radical-ion salts at a high pressure, which was explained by a shift of the equilibrium between the monomeric and dimeric forms of the $TCNQ^-$ anions[132]. A similar bathochromic shift was observed also for the charge-transfer band[133] owing to the decrease of the distance between the $TCNQ^-$ anions on compression. It was found that the effect of the magnetic field is similar to that of the solvent on the absorption spectra of salts on passing from a non-polar to a polar solvent[134].

The study of the infrared spectra of the TCNQ complexes and radical-ion salts showed that the spectrum of acceptor, both neutral[135] and anionic[136,137], persists in both cases. The $TCNQ^-$ vibrations differ from those of TCNQ by a comparatively slight frequency shift. The frequency of the C≡N vibrations shifts by 25–30 cm^{-1} towards lower values, which is characteristic of all TCNQ salts and the band itself usually splits into 3–4 components, separated from one another by 10–15 cm^{-1}. The type B_{2u} and B_{3u} C=C vibration frequencies differ from one another much more markedly than for TCNQ: 1515 and 1590 cm^{-1} instead of 1540 and 1545 cm^{-1}.[127] A broadening of the bands in the range 1100–1600 cm^{-1} is characteristic of highly conducting TCNQ salts and the half-width of the bands can reach 150 cm^{-1}.[137] A study of the infrared spectra of the complexes and the radical-ion salts in the range 20–400 cm^{-1} showed that there is an absorption head in the region of 40 cm^{-1}, interpreted as corresponding to direct allowed transitions from the ground to the excited band, which is probably also the conductivity band[138].

It is noteworthy that molecular vibrations which are forbidden in free molecules can frequently become allowed in charge-transfer complexes. Thus the band (1565 cm^{-1}) due to the stretching vibrations of the C=C bond in TCNQ becomes allowed in the 1:1 TCNQ–hexamethylbenzene complex and the band (1296 cm^{-1}) due to the stretching vibrations of the C–CH_3 bonds of hexamethylbenzene appears in the spectrum of the 1:2 complex[135].

The use of NMR for the investigation of TCNQ complexes is of interest. Thus, by measuring the chemical shift of the hexamethylbenzene protons in the complex with TCNQ relative to the positions of the signals for the pure donor, it was possible to determine the equilibrium constant for this complex[139]. An NMR study of highly conducting TCNQ salts[140,141] demonstrated the localised nature of the electronic states in the salts at low temperatures.

3. Electrical and Magnetic Properties

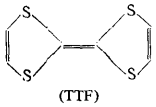
TCNQ complexes as well as the complexes of other well known acceptors as a rule exhibit semiconducting properties. The temperature variation of their conductivity can be described by the equation

$$\sigma = \sigma_0 e^{-\epsilon/kT},$$

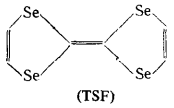
where σ is the conductivity at a given temperature T (on the absolute scale), σ_0 a number characterising the conductivity of $T = \infty$, k the Boltzmann constant, and ϵ the thermal activation energy.

The first studies on TCNQ complexes were in fact devoted to the investigation of the electrical properties of these compounds[142,143]. Most of the data published since that time have been summarised in the monograph of Gutmann and Lyons[144], where the properties of TCNQ complexes are discussed among those of other organic semiconductors. The electrical properties of TCNQ complexes are also discussed in two other reviews, one of which is likewise devoted to organic semiconductors[145] and the other deals with the problem of high-temperature superconductivity[146].

The resistivities of TCNQ complexes were quoted previously in Tables 2, 4, 5, 7, and 8. The TCNQ complexes of tetrathiofulvalene (TTF),[107] *trans*-*cis*-dimethyl-TTF,[147] tetramethyl-TTF,[148] and tetraselenofulvalene (TSF)[106] exhibit the highest conductivities.



(TTF)



(TSF)

While the mechanism of conduction by TCNQ complexes with high resistivities has been fairly thoroughly investigated[144] (these complexes differ little from those of other widely used acceptors), the elucidation of the mechanism of conduction in highly conducting TCNQ salts is at present the most interesting task (salts with "metallic conductivity" will be discussed separately).

Hitherto most studies have dealt with the synthesis of new TCNQ complexes[49,62,63,66,147-150], which are as a rule characterised by their conductivities. At the same time more thorough studies are being made of the electrical properties of TCNQ complexes synthesised previously. Thus two activation energies (for temperatures below and above 400 K) have been obtained from the temperature variation of the conductivity of single crystals of simple alkali metal salts of TCNQ in the temperature range 300 to 540 K. A change from hole to electronic conductivity was observed for the sodium and potassium salts when the activation energy changed[151], which clearly indicates the occurrence of two conduction mechanisms in these salts. A first-order phase transition in the range 350–400 K was recently observed[152] for the same salts, which may be associated with the change in the activation energy for conduction. A more complex change in activation energy was found for the triethylammonium$^+$-$(TCNQ)_2^-$ salt[153,154]; here the activation energies pass through a maximum at 222 K. The activation energies for conduction, determined for different crystallographic directions in single crystals of triphenylmethylphosphonium$^+$-$(TCNQ)_2^-$[155,156] and triphenylmethylarsonium$^+$-$(TCNQ)_2^-$[157] also differ.

Thus the activation energy may depend on the temperature and the direction of motion of the carriers, which is probably associated with a more complex mechanism of conduction than in the usual semiconductors. Studies on the changes in conductivity and in activation energy for conduction in TCNQ salts as a function of pressure are of interest from this standpoint[158-160]. As a rule the conductivity increases with increase of pressure, while the activation energy falls.

It is significant that, even at the highest pressures, metallic conductivity was not observed in the salts[159], i.e. the overall variation of the conductivity with temperature remained characteristic of semiconductors.

In order to investigate the conduction mechanism, it is important to determine the type of charge carriers and their mobility. However, the mobilities found in measurements of the Hall effect for single crystals of a number of highly conducting TCNQ salts[161-163] are low (0.6 to 0.004 $cm^2 V^{-1} s^{-1}$) and do not permit preference to be given to any one conduction mechanism.

The thermo-e.m.f.'s of a number of TCNQ salts have been measured[161,164,165]. The sign of the thermo-e.m.f. of highly conducting quinolinium, acridinium, and *N*-methylphenazinium salts indicates electronic conductivity, while that of the complex triethylammonium salt indicates hole conductivity. It is therefore impossible to reach unambiguous conclusions concerning the mechanism of conduction in TCNQ salts with low resistivities. Whereas some investigators discuss the observed conductivities and activation energies within the framework of the band model[153], others postulate a jump mechanism[165,166]. The latter is probably preferable, since the majority of data indicate the presence of a system of localised current carriers, the motion of which at any stage must include a thermally activated jump. At least the low-temperature conductivities of a number of highly conducting TCNQ salts are described satisfactorily by this model[167-170].

It is noteworthy that the discrepancy between the electrical properties of TCNQ complexes, frequently found in studies by different investigators, can be accounted for by the lack of purity criteria for these compounds. Thus the *N*-methylphenazinium salt of TCNQ synthesised from highly pure components, exhibits a higher conductivity at an elevated temperature than stated previously and at low temperatures (below 100 K) its conductivity is ten times lower than that described in an earlier investigation[171]. Another cause is a marked influence of gaseous impurities, which may play a significant role in measurements on polycrystalline specimens. Thus, when simple alkali metal radical-ion salts are heated *in vacuo*, the conductivity falls, the activation energy for conduction increases, and the thermo-e.m.f. changes sign[161,172], which can be explained by the influence of atmospheric oxygen, playing the role of an electron-accepting impurity.

The magnetic properties of TCNQ complexes are also being vigorously investigated. Although molecular complexes and simple radical-ion salts are as a rule diamagnetic, the complex salts are paramagnetic. A qualitative correlation may be traced between the concentration of unpaired spins and the conductivity of TCNQ complexes (Table 11).[112]

The presence of an ESR signal of TCNQ complexes indicates a radical-ion nature of the complex, a phenomenon which is frequently used to determine the type of intermolecular bond (i.e. whether the given substance is a molecular complex or a radical-ion salt)[173,174].

The study of the ESR spectra of a large number of radical-ion salts[175-180] showed that complex TCNQ salts give rise to a fairly intense ESR signal; the number of unpaired spins per complex molecule varies from 1.5 to 10^{-2}. For simple salts, the concentration of free spins is much lower, which can be explained by the very strong

pair interaction between ions of the same kind. On the other hand, in the crystal lattices of highly conducting TCNQ salts the ions form infinite stacks with the same interionic distances; such salts as a rule give rise to an intense ESR signal. Complex salts with a low conductivity have a weak ESR signal for the same reasons as in the case of simple TCNQ salts.

Table 11. The number of unpaired spins per donor–acceptor pair in TCNQ complexes.

Complex	Number of unpaired spins per complex molecule	Conductivity at 300 K, Ω^{-1} cm^{-1}
N-Methyl-2,3-benzoquinolinium$^+$-$(TCNQ)_2^-$	1.3	2.8×10^{-2}
N-Methyl-3,4-benzoquinolinium$^+$-$(TCNQ)_2^-$	0.05	4.3×10^{-3}
N-Methyl-7,8-benzoquinolinium$^+$-$(TCNQ)_2^-$	0.056	8.0×10^{-3}
Hexamethylbenzene-TCNQ: single crystal	7.5×10^{-4}	–
polycrystalline powder	1.8×10^{-3}	–
1,2-Benzopyrene-TCNQ: single crystal	4.0×10^{-5}	–
polycrystalline powder	1.8×10^{-3}	1.9×10^{-12}
3,4-Benzopyrene-TCNQ: polycrystalline powder	6.3×10^{-4}	2.4×10^{-11}

TCNQ complexes with benzidine, which form clathrate compounds with solvents[51], constitute an interesting example of the mechanical generation of spins. The crystals of the complex are not paramagnetic both in the presence and absence of a solvent. However, when the crystals of a complex containing the solvent are ground to a powder, a strong ESR signal ($g = 2.0027$) is observed.

A careful study of the ESR spectra of various TCNQ salts over a wide range of temperatures showed that the behaviour of one set of triplets in the spectra is independent of temperature and is due to impurities and defects in the crystal lattice. Those in another set represent thermally excited triplet states, the concentration of which depends on temperature[181,182]. Similar results were obtained in a study of the dynamics of the nuclear polarisation of protons in simple alkali metal salts of TCNQ[183] and in the complex triphenylmethylarsonium salt of TCNQ.[184] Triplets of a new type, existing in the temperature range from 4 to 80 K, were observed in the ESR spectrum of the latter salt[182]. The authors suggest that this triplet is formed by two unpaired electrons delocalised over the neighbouring chains of $TCNQ^-$ anions.

The occurrence of a phase transition in the triphenylmethylphosphonium$^+$-$(TCNQ)_2^-$ and triphenylmethylarsonium$^+$-$(TCNQ)_2^-$ salts was confirmed with the aid of ESR.[185]

The method of double electron–electron resonance has been used recently to investigate triplet states[186,187]. The study by this method of the triplet excitons in TCNQ ion-radical salts of triphenylmethylphosphonium and cyanine dyes in the temperature range 150–350 K demonstrated that the formation of triplets is an activated process.

The temperature variation of the magnetic susceptibilities of simple[188,189] and complex[190] TCNQ salts and of salts with high[191] and moderate[192,193] conductivities has been studied. Whereas at high temperatures the magnetic susceptibility may increase slightly or fall with decrease of temperature, it increases sharply starting from 50 K. The low-temperature increase of suceptibility is not associated with the presence of paramagnetic impurities and reflects the intrinsic properties of the complexes.

We may note that the magnetic properties of TCNQ salts, as well as their electrical properties, depend on their structures. Thus, when the highly conducting ($\sigma = 380\ \Omega^{-1}$ cm^{-1}) *N*-methylphenazinium salt of TCNQ, which gives rise to a strong ESR signal, was recrystallised, a non-magnetic phase with $\sigma = 7.67 \times 10^{-5}\ \Omega^{-1}$ cm^{-1}) was obtained; by crystallisation, it can be reconverted into the initial form[194].

Yet another aspect of studies of the electrical properties of TCNQ complexes should be noted. In 1964 Little suggested[195,196] the possibility of an exciton mechanism of superconductivity in which there is attraction between conductivity electrons owing to exciton exchange (electronic excitations) and not phonon exchange. According to certain estimates, an exciton mechanism should lead to much higher temperatures of the superconductivity transition (above 300 K).

The manifestation of an exciton superconductivity mechanism requires a certain combination of two subsystems: one conducting and another dielectric with the appropriate exciton spectrum. Complex radical-ion salts proved to be promising for the synthesis of systems satisfying the requirements of Little'e model, since infinite stacks of anions in the highly conducting salts are effective conducting systems and polarisable cations can constitute dielectric systems. TCNQ salts of dyes were in fact synthesised for this purpose[58,59,197,198]. These salts did not exhibit superconductivity, but behaved as typical organic semiconductors; this was readily accounted for after the investigation of their crystal structure which does not contain infinite uniform stacks of TCNQ anions.

A sensational report of an extremely high conductivity of the TCNQ–tetrathiofulvalene (TTF) complex (10^6 Ω^{-1} cm^{-1}), observed at 60 K, appeared recently; on cooling from 300 to 60 K the conductivity, being of the metallic type, increased by a factor of 500.[199] The authors regarded this conductivity as a result of fluctuations leading to temporary transitions to the superconducting state of the complex near the structural transition temperature. This report led immediately to vigorous studies on this compound. Repeated measurements of the conductivity of the complex, carried out by different investigators[200–202], including measurements by the contactless method at high frequencies, failed to confirm such a high increase of conductivity; at 60 K it increases by a factor of 10 to 150, probably depending on the purity of the test specimen.

Conductivity of the metallic type has now been observed for a fairly large set of TCNQ complexes (Table 8), which can be divided into two groups. A low phase transition temperature (<100 K), a symmetrical cation, and a high conductivity are characteristic of the first group (complexes with tetraselenofulvalene, tetrathiofulvalene, and tetrathiotetracene). In this group the TTF–TCNQ complex has been investigated in greatest detail; using it, we shall trace the changes in the properties of such complexes as a function of temperature.

The study of the crystal structure of the TTF–TCNQ complex at room temperature showed that, as for all highly conducting TCNQ salts, infinite columns of anions and cations with interplanar distances of 3.17 Å between neighbouring anions and 3.47 Å between neighbouring cations are characteristic of this complex[107]. At 40 K the structure of the complex remains unchanged and there is only a slight decrease of the distances between the neighbouring anions and cations, to 3.11 and 3.43 Å respectively[203].

In terms of the variation of its thermo-e.m.f., the TTF–TCNQ complex behaves as a metal in the temperature range from 140 to 56 K; at 56 K the Seebeck coefficient becomes abruptly zero, changing sign at lower temperatures [204].

The study of the magnetic properties of the complex showed [205] that the substance is diamagnetic at $T < 20$ K and paramagnetic at $T > 20$ K, the magnetic susceptibility increasing monotonically with increase of temperature to 359 K. The spectroscopic properties of the TTF–TCNQ complex have been investigated: the polarisation absorption spectra [206] and the reflection spectra of single crystals [207]. The overall form of the spectrum is typical for TCNQ radical-ion salts. A plasma absorption head was observed at 1.4 μm. The transition to the dielectric state below 60 K was confirmed also by heat capacity measurements [208]. On the basis of all the above findings, it is suggested that a metal–dielectric transition of the pyerls (structural) type probably occurs in this group of salts [209].

The second group includes the simple *N*-methylphenazinium salt of TCNQ and the complex quinolinium$^+$-$(TCNQ)_2^-$ and acridinium$^+$-$(TCNQ)_2^-$ salts. A comparatively high-temperature metal–dielectric transition has been observed (from conductivity measurements; below the transition temperature the conductivity is of the semiconductor type) for these salts, which contain asymmetric cations. The study of other properties of the salts—magnetic susceptibility [210], heat capacity [211], and optical properties [212]—demonstrated the occurrence of a phase transition at 14 K for the quinolinium$^+$-$(TCNQ)_2^-$ salt and in the region of 10–30 K for the *N*-methylphenazinium salt of TCNQ. It is suggested that at low temperatures ($<\sim$15 K) these salts are in the state of a disordered Mott–Hubbard dielectric, which behaves as a one-dimensional disordered metal above the phase transition temperature ($\sim$15–$\sim$200 K). [212] The non-metallic type of temperature variation in this temperature range may be associated with the spatial localisation of electrons, arising owing to the disorder in the crystal lattice, which in turn can be accounted for by the asymmetry of the cations [210].

Although all known TCNQ salts with the metallic type of conductivity are converted into dielectrics at a low temperature, the question of the possible superconductivity of these compounds (for example, near the phase transition temperature) still remains unresolved. The instability of such quasi-one-dimensional electronic systems had been demonstrated theoretically before the systems were obtained experimentally [209] and further studies on these salts should show whether or not they are capable of superconductivity. Furthermore, these salts constitute an excellent model of a quasi-one-dimensional metal and the study of such systems is extremely interesting from the standpoint of solid state physics.

In connection with this problem, mention may be made of several other investigations. It has been shown that organic compounds, including TCNQ, influence the temperature of the transition to the superconducting state in thin metallic films [213]. Thus TCNQ sputtered onto a thin vanadium film (50–200 Å) reduced the temperature of its transition to the superconducting state, while electron-donating compounds, for example anthracene, increased it by 0.05–0.1 K. The material obtained by the simultaneous sputtering of aluminium and TCNQ behaves similarly [214].

In conclusion mention should be made of studies undertaken to create conducting polymeric materials. Using various polymeric molecules as electron donors, TCNQ complexes and radical-ion salts have been obtained. A large number of materials of this type have been patented [215–222], their resistivities amounting to 100–1000 Ω cm. Another method for the synthesis of conducting materials involves the addition of the lithium salt of TCNQ to a polymer containing amino-groups. Whereas the initial polymers have resistivities of about 10^{16} Ω cm, the materials obtained by this procedure have a resistivity of about 10^8 Ω cm, although the amount of added salt does not exceed 5%. [223–225].

A review published recently [226] is devoted to complexes of polymeric donors with various acceptors, including TCNQ. We shall merely mention that the polymeric complexes have still been very little investigated and a large field of research awaits investigators in this connection. The electrical [227–230] and magnetic [231] properties of polymeric TCNQ complexes are being mainly studied at the present time. The first attempts are being made to relate the electrical properties of the complexes to their structures [232]. If TCNQ complexes do find applications, they are most likely to be complexes based on polymeric donors.

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We have examined the principal aspects of research on TCNQ carried on at the present time. The study of reactions of TCNQ with nucleophilic agents, via intermediate one-electron oxidation, is the most interesting and promising in the chemical sense; such organic reactions have so far been inadequately investigated. The stable $TCNQ^-$ radical-anion is also an interesting object of study in reactions with radical and electrophilic reagents.

The electrical properties of TCNQ complexes have been primarily investigated in studies on the properties of crystals with conductivity of the metallic type. The problem of the possible superconductivity of such systems is extremely important. Crystals of this kind are also interesting from the standpoint of the physical properties of a quasi-one-dimensional electronic system.

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