

ORGANIC SEMICONDUCTORS: SIMPLE AND COMPLEX SALTS
OF 1-METHYL-3-ALKYLIMIDAZOLIUM
7,7,8,8-TETRACYANO-*p*-QUINODIMETHANE

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By metathesis between lithium salts of 7,7,8,8-tetracyano-*p*-quinodimethane and 1-methyl-3-alkylimidazolium bromides, simple radical salts were prepared whose specific electrical conductivity values are $c. 10^{-7} - 10^{-3}, \Omega^{-1} m^{-1}$, according to the donor structure. Combining these salts with neutral 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ⁰) gave complex salts with an electrical conductivity higher by 7–3 orders of magnitude which increases monotonically with increasing volume of the alkyl group. The compounds are stable in anhydrous conditions also in presence of oxygen, and if irradiated by daylight. The rate constant of hydrolysis of these salts is proportional to the water content in solution and inversely proportional to the content of neutral TCNQ⁰ in the simple radical salt. The hydrolysis is predominantly activated by light absorbed by the decomposition products.

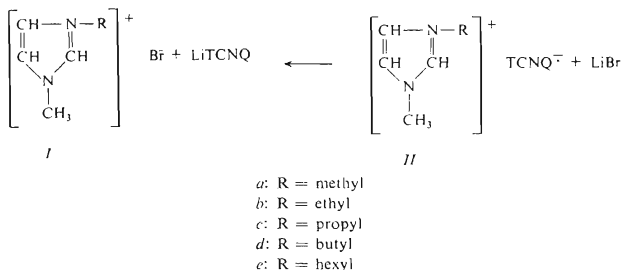
The unusually high conductivity of the solid complex of tetrathiofulvalene (TTF) with 7,7,8,8-tetracyano-*p*-quinodimethane¹ (TCNQ) has aroused interest in the preparation of further conductive compounds and in a study of their physical properties. In recent years, a whole number of TCNQ complexes have been prepared², many of which possess conductivity of metallic character. The high conductivity is assigned to the segregated stacks order which underlies a strong anisotropic behaviour. The mechanism of electrical conductivity of TCNQ salts is affected by many factors, and some effects, such as *e.g.* the symmetry and polarization of molecules^{1,3}, steric factors⁴, ionization potential of donors⁴, electron transfer between the acceptor and donor^{4,5} *etc.* are still the topic of many discussions.

This paper reports the preparation of semiconductive simple and complex TCNQ salts containing 3-alkyl substituted 1-methylimidazoles as cations, their electrical conductivity values and the activation energies, and an investigation of their chemical stability as a function of the water content in the solvent.

EXPERIMENTAL

Chemicals

Simple ion-radical TCNQ salts based on substituted imidazole *II* were prepared by metathesis between salts of imidazole *I* and TCNQ using the equation



Bromides *Ia*, *Ib*, and *Ie* were prepared by a reaction between the respective 1-alkylimidazoles and methyl bromide. *Ic* and *Id* were obtained by a reaction between 1-methylimidazole with the respective *n*-alkyl bromide. From a complete quaternization of *Ib*, *Id* and *Ic*, alkyl bromide had to be in an amount exceeding several times the stoichiometric one. The reactions were carried out in anhydrous ether at the boiling point under reflux for 1 h. After that, the reaction mixture was left to stand overnight, and the product was isolated. On cooling, *Ia* (m.p. 384–386 K), *Ib* (m.p. 337–339 K) crystallized as white compounds. In the other cases bromides were light-brown in colour, and oily. In the isolation of oily products ether was evaporated, and the residue was stirred several times in a small amount of anhydrous benzene and evaporated at reduced pressure. The temperature of the heating bath during this operation was maintained below 313 K. Compounds *I* are strongly hygroscopic and must be kept in an anhydrous solution, during both the preparation and further treatment. The results of the reactions are summarized in Table I.

The simple radical salts *II* were prepared by metathesis so that a solution of the respective bromide of imidazole *I* in absolute ethanol was added dropwise to an equivalent amount of a saturated solution of LiTCNQ in absolute ethanol at the boiling point of the solvent. After stirring for 30 min at the reaction temperature, the mixture was cooled and product *II* which crystallized was recrystallized several times from absolute ethanol. Salts *II* are crystalline compounds, violet-blue in colour. Elemental analysis showed that only stoichiometric (1 : 1) simple radical salts were obtained by the metathesis. The results of the reactions are summarized in Table II.

Complex radical salts, the composition of which may be expressed by formula *III* (indexes *a–e* are the same as for *I* and *II*), were prepared so that corresponding amounts of the simple salt *II* and of neutral TCNQ⁰ were mixed together and dissolved while hot in acetonitrile without the access of air. The solvent was evaporated, and salts *III* were dried in vacuum ≈ 1 Pa for 48 h.

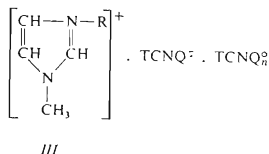


TABLE I
1-Methyl-3-alkylimidazolium bromides (I)

Compound	Imidazole mol	Alkyl-bromide mol	Yield %	Calculated/Found			
				% C	% H	% N	% Br
<i>Ia</i>	1.0	1.1	91	33.92	5.13	15.82	45.13
				33.76	5.34	15.47	44.78
<i>Ib</i>	1.0	3.0	72	37.72	5.80	14.66	41.82
				37.31	5.93	14.64	41.49
<i>Ic</i>	1.0	1.1	90	40.99	6.38	13.66	38.97
				40.73	6.58	13.54	39.28
<i>Id</i>	1.0	2.0	88	43.85	6.90	12.78	36.47
				43.13	6.80	12.41	36.33
<i>Ie^a</i>	1.0	2.0	87	48.59	7.75	11.33	32.33
				48.30	7.82	11.37	31.67

^a Prepared (in contrast with the reported procedure⁶) from sodium salt of imidazole by a reaction with hexyl bromide in DMF in a sealed ampoule at 353 K within 6 h, and rectified (b.p. = 395.0—395.5/0.8 kPa).

TABLE II
Simple radical salts (II)

Compound	Yield %	M.p. ^a K	Calculated/Found		
			% C	% H	% N
<i>IIa</i>	56	447—450	67.78	4.34	27.88
			67.49	4.49	27.57
<i>IIb</i>	51	416—419	68.54	4.80	26.66
			68.40	4.87	26.67
<i>IIc</i>	61	432—434	69.28	5.21	25.51
			69.18	5.23	25.52
<i>IId</i>	71	427—429	70.01	5.56	24.43
			70.04	5.66	24.41
<i>IIe</i>	38	397—399	71.13	6.24	22.63
			70.87	6.11	22.94

^a Kofler block, uncorrected.

Electrical Conductivity

The specific electrical conductivity was measured by the four-electrode method⁷ on pressed polycrystalline pellets. The pellets, 13 mm in diameter, were pressed in a Perkin-Elmer die under 0.66 MP for 120 s from 150 mg of the material, well ground in an agate dish. The pressing surfaces of the die were coated with a teflon film, which prevented cracking of the pellets. Four gold electrodes, surface area 1 mm², were vacuum deposited on the periphery of the pellet. Contact was accomplished by means of silver conductive paste. For the purposes of measurement, the discs were placed on a sapphire support. The thermal contact was provided with silicone grease. The measurement was carried out in an Air-Products (USA) cryostat at a pressure of $<10^{-4}$ Pa. The current passing through the sample was measured with a Keithley 601 battery electrometer (USA), the voltage was determined with a Keithley 616 electrometer (USA). The temperature was stabilized with an accuracy of ± 0.1 K.

Chemical Stability

In the investigation of the course of hydrolysis of TCNQ salts the stock solutions were thermostated at a chosen temperature with an accuracy of ± 1 K. The samples were taken in chosen time intervals, and the electron spectra were recorded with a Cary 14 (USA) spectrophotometer. Irradiation was performed at a distance of 20 cm, either using a universal lamp UV-CAMAG (Switzerland), or by means of a mercury discharge tube HBO-200 (GDR) with interference filters. The number of photons incident on the cell was measured with an EG & G 580 radiometer (USA). The thermal radiation was filtered with a 10 cm aqueous filter.

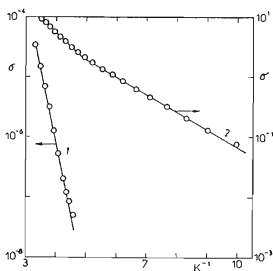


FIG. 1

Dependence of electrical conductivity on reciprocal temperature. 1 Simple salt *III*d, 2 complex salt *III*d ($n = 1.0$)

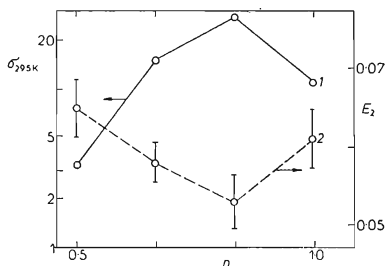


FIG. 2

Dependence of specific conductivity 1 and of its activation energy E_2 (eV), 2 on mass amount n of neutral TCNQ⁰ corresponding to one mol of TCNQ⁻ of complex salt *III*d

RESULTS AND DISCUSSION

Electrical Conductivity

All the radical salts prepared in this study have a semiconductive character. A typical temperature dependence of electrical conductivity for salts *II*d and *III*d ($n = 1$, cf. structure *III*) is shown in Fig. 1. The specific conductivity values σ_{295K} (Ωm)⁻¹ and its activation energies E_1 , E_2 , where E_1 is the activation energy of electrical conductivity in the relation $\sigma = \sigma_0 \exp(-E/kT)$ in the "high-temperature range" ($10^3/T$ is c. $3-5 \text{ K}^{-1}$), E_2 is the same quantity in the "low-temperature range" ($10^3/T > 5.5 \text{ K}^{-1}$), for simple salts *II* and complex salts *III* are listed in Table III. The specific conductivity of simple salts at room temperature is lower than that of the corresponding complex salts by 3-7 orders of magnitude (for $n = 0.5$). An addition of neutral molecules TCNQ⁰ increases the conductivity still further. For instance, for the complex salt *III*d the conductivity reaches its maximum at $n = 0.85$. For the same n the activation energy of conductivity reaches its minimum as documented by Fig. 2. The conductivity of the simple salts reaches its minimum for *II*c ($R = \text{propyl}$) and increases both for the other, sterically bulkier, and for smaller substituents (Fig. 3a). The conductivity of complex salts increases monotonically with increasing volume of the substituent. At the same time, the activation energy of conductivity decreases, and for salts *III*c, *III*d and *III*e it is already so low that the dc

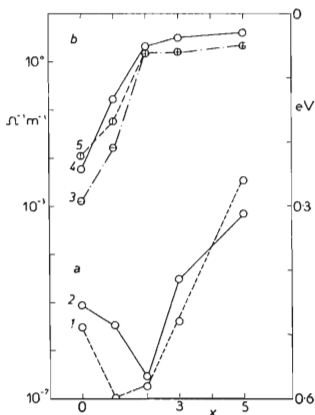


FIG. 3

Dependence of specific electrical conductivity 2, 4 and of its activation energy E_1 1, 3 or E_2 (eV) 5 on the number of methylene groups (x) in the donor *II* ($R = (\text{CH}_2)_x\text{—CH}_3$) (a) of simple and (b) complex ($n = 0.5$) salts

measurements do not allow us to determine if the activation energy involved is that of the conductivity of the material itself or corresponds to the interparticle boundaries⁸.

Chemical Stability

The effect of the surrounding medium, *i.e.*, of moisture and light on the stability of salts was mainly studied with *IIc* (as model) in acetonitrile solutions freed from oxygen by flushing with nitrogen during 30 min. The stability was evaluated from a decrease in the absorbance at 840 nm (Fig. 4), a characteristic band of the anion-radical TCNQ^- . The half-width of the band remained constant during the measurement. The rate constant K was determined from $K = \ln A/t$, in which A is absorbance and t is time. In anhydrous acetonitrile, neither in the dark nor in the daylight, not even in presence of oxygen (solutions flushed with dry oxygen for 30 min) could

TABLE III
Specific electrical conductivity and activation energy of conductivity of radical salts *II* and *III*

Compound	n^a	$\sigma_{295K} \Omega^{-1} \text{m}^{-1}$	E_1 eV	E_2 eV
Simple salts				
<i>IIa</i>	0	$8.3 \cdot 10^{-6}$	0.49(1) ^b	^c
<i>IIb</i>	0	$3.7 \cdot 10^{-6}$	0.60(1)	^c
<i>IIc</i>	0	$2.9 \cdot 10^{-7}$	0.58(1)	^c
<i>IId</i>	0	$3.4 \cdot 10^{-5}$	0.48(1)	^c
<i>IIE</i>	0	$7.7 \cdot 10^{-4}$	0.26(1)	^c
Complex salts				
<i>IIIa</i>	0.50	$6.6 \cdot 10^{-3}$	0.29(1)	0.22(1)
<i>IIIb</i>	0.50	$1.8 \cdot 10^{-1}$	0.21(1)	0.17(1)
<i>IIIc</i>	0.50	$2.2 \cdot 10^0$	0.058(1)	0.058(1)
<i>IIId</i>	0.50	$3.3 \cdot 10^0$	0.065(1)	0.065(1)
<i>IIIe</i>	0.65	$1.5 \cdot 10^1$	0.092(2)	0.058(1)
<i>IIIe</i>	0.85	$2.9 \cdot 10^1$	0.053(1)	0.053(1)
<i>IIIe</i>	1.00	$1.1 \cdot 10^1$	0.101(2)	0.061(1)
<i>IIIe</i>	0.50	$4.2 \cdot 10^0$	0.053(1)	0.053(1)

^a Index in structure *III*; ^b numbers in brackets denote the range R of the values found; *e.g.*, 0.49(1) means that $R = 0.01$; ^c not measured.

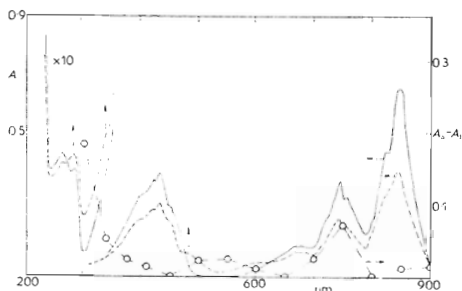


FIG. 4

Absorption curves of simple radical salt *IIc* in ——— anhydrous acetonitrile ($c(\text{IIc}) = 2.74 \cdot 10^{-4} \text{ mol l}^{-1}$), ----- 50% aqueous acetonitrile, concentration the same, after standing in the dark for 16 h, $T = 296 \pm 2 \text{ K}$; ····· dependence ($A_d - A_1$) vs λ , A_d is absorbance at 840 nm for a solution kept in the dark, A_1 is absorbance at 840 nm after irradiation of solution. The values have been corrected to the same number of protons incident on the cell

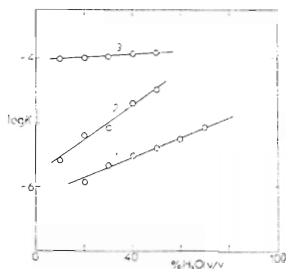


FIG. 5

Dependence of the rate constant of hydrolysis (in s^{-1}) of simple radical salt *IIc* on water content in acetonitrile, $T = 298 \pm 1 \text{ K}$; 1 in the dark, $c(\text{IIc}) = 3.29 \cdot 10^{-4} \text{ mol l}^{-1}$, 2 irradiated with light $\lambda = 366 \text{ nm}$, $c(\text{IIc}) = 3.59 \cdot 10^{-4} \text{ mol l}^{-1}$, 3 irradiated with light $\lambda = 254 \text{ nm}$, $c(\text{IIc}) = 3.19 \cdot 10^{-4} \text{ mol l}^{-1}$

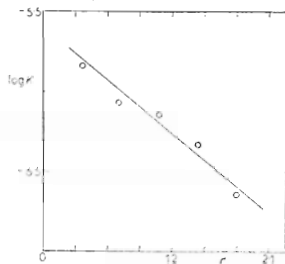
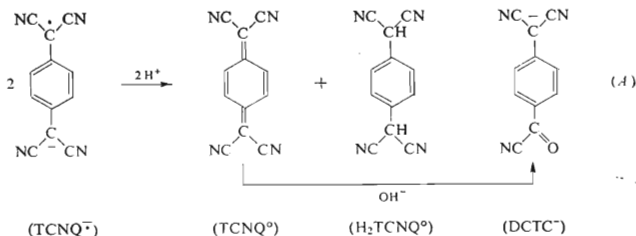


FIG. 6

Dependence of the rate constant of hydrolysis (in s^{-1}) of simple radical salt *IIc* on the ratio (r) of the mass amount of TCNQ^0 to that of TCNQ^- in *IIc* in 50% aqueous acetonitrile in the dark, $T = 299 \pm 1 \text{ K}$, $c(\text{IIc}) = 3.11 \cdot 10^{-4} \text{ mol l}^{-1}$

any change in the absorbance at 840 nm be perceived at room temperature, even after 200 h. This finding is however changed if water is present. The rate of hydrolysis in water (in the absence of oxygen) is directly proportional to the water content in acetonitrile (Fig. 5, dependence 1). On irradiation, the rate of hydrolysis increases (Fig. 5, dependences 2 and 3).

In order to find out which wavelength of radiation affects the hydrolysis most, we recorded the spectral course of the rate of hydrolysis of salts *IIc* in 50% aqueous acetonitrile freed from oxygen as a change in the absorbance at 840 nm depending on time. The results are given in Fig. 4 as the dependence of $(A_d - A_1)$ vs λ , in which A_d is the absorbance at 840 nm of the solution kept in the dark, A_1 is the absorbance after irradiation of the solution, λ is the wavelength of light. As can be seen, with the exception of the wavelength of $\lambda \sim 750$ nm, radiation absorbed by the anion radical TCNQ^- has no major influence on the rate of hydrolysis. A much stronger effect is exerted by radiation absorbed by the products of hydrolysis ($\lambda = 280, 337, 480$ nm), especially in the UV range of the spectrum.



The final products of hydrolysis of salts containing TCNQ^- are α,α -dicyano-*p*-toluoylcyanide anion (DCTC^-) and *p*-phenylenedimalononitrile^{9,10} (H_2TCNQ^0). DCTC^- arises through an intermediate which is neutral TCNQ^0 . The excess of neutral TCNQ^0 , as observed with complex salts, though not preventing the reaction TCNQ^0

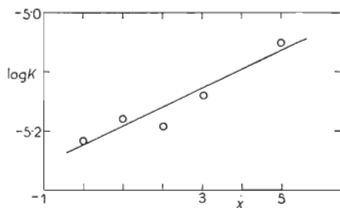


FIG. 7.

Dependence of the rate constant of hydrolysis (in s^{-1}) of simple radical salts *II* ($\text{R} = (\text{CH}_2)_x\text{—CH}_3$) on the number of methylene groups (x) in the donor in 50% aqueous acetonitrile in the dark, $T = 307 \pm 1$ K, $c(\text{II}) = 3.30 \cdot 10^{-4} \text{ mol l}^{-1}$

+ OH⁻ → DCTC⁻, reduces the rate of degradation of the anion-radical TCNQ⁻. Indeed, as can be seen in Fig. 6, the logarithm of the rate constant of hydrolysis is inversely proportional to the ratio (*r*) of the mass amount of TCNQ^o to that of TCNQ⁻ in a simple radical salt. Steric changes performed on the donor in an extent indicated in this study have no basic influence on the stability of salts towards water (Fig. 7). The rate of hydrolysis insignificantly increases with the size of the alkyl substituent.

The presence of DCTC⁻ was proved by the character of the electron spectrum of a product obtained after salt *Iic* was left to stand for 16 h in 50% aqueous acetonitrile with typical bands at 280, 337 and 480 nm (*cf.*⁹). Also the infrared spectrum of the product of hydrolysis obtained by evaporation of the solvent after salt *Iic* has been left to stand for several months in aqueous acetonitrile indicates the presence of DCTC⁻. The spectrum contained, along with other bands, a strong carbonyl band at 1 650 cm⁻¹, a band of *p*-substituted phenyl at 830 cm⁻¹ and nitrile bands at 2 200 and 2 150 cm⁻¹. Since the salts were stable both in anhydrous solution and in presence of oxygen, we favour the opinion that DCTC⁻ arises rather by hydrolysis of the anion-radical TCNQ⁻ than by its direct oxidation with air oxygen, as has been observed in a study of the degradation of TCNQ salts in the solid state^{11,12}.

Thus, a new group of conductive organic salts of the type 1-methyl-3-alkylimidazolium 7,7,8,8-tetracyano-*p*-quinodimethane was prepared. The electrical conductivity in polycrystalline pellets amounts to $7.7 \cdot 10^{-4} (\Omega\text{m})^{-1}$, and the activation energy is higher than 0.26 eV. The presence of neutral TCNQ^o raises the conductivity of these compounds up to $2.9 \cdot 10^1 (\Omega\text{m})^{-1}$, while the activation energy drops to *c.* 0.05 eV. The compounds are stable in an anhydrous medium also in presence of oxygen and if irradiated.

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