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Tetracyanoquinodimethan Derivatives of Cyanine Dyes

A Model for Organic Superconductors?

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Abstract—Recently, Little suggested that certain organic materials could act as superconductors at temperatures much higher than the conventional inorganic superconductors. In view of the complicated nature of the proposed compounds it was felt that this idea could only be tested directly if a simpler system could be found. For that purpose a number of TCNQ derivatives of cyanine dyes were prepared and their electrical conductivities were measured in a simple way. It turned out that their conductivities (2.5×10^{-3} to $8 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$) are comparable to those of other TCNQ derivatives. There were no indications of an enhanced conductivity due to the presence of the highly polarizable cyanine cations.

Introduction

In 1964, Little^{1,2} proposed that certain organic materials could act as superconductors with transition temperatures at room temperature or higher. It was suggested that conjugated polymer chains carrying appropriate substituents would show the desired behavior.

In latter publications³⁻¹¹, Little's theoretical approach was discussed and experimental work touching on the subject was published by McConnell¹² who showed that the superconductivity in thin vanadium films could be influenced by a layer of organic material deposited on the vanadium surface. However, these experiments concerned a well known metallic superconductor and do not provide evidence in support of Little's concept of completely organic superconductors.

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In two Patent Applications¹³, methods are described for the synthesis of materials according to Little's idea. Although it is claimed that these compounds are organic superconductors, no experimental evidence whatsoever is presented in support of these claims.

Little's requirements for the substituents on the polyene chain are that they "have a low lying excited state such that transitions from the ground state to the excited state correspond classically to an oscillation of charge from end to end of the molecule." Specifically he recommends organic dye-like substituents.

The essential feature of this proposal—the combination of highly polarizable groups with a polymer chain which can serve as a conductive path—was further discussed by LeBlanc.¹⁴ However, a chain carrying cyanine dye-like substituents would be very difficult to synthesize and the absence of adequate samples would prevent actual testing of Little's proposal. Therefore another, more readily accessible, model system should be selected.

In the search for model compounds it was realized that in highly conductive, salt-like, derivatives of 7,7,8,8-tetracyanoquinodimethan (TCNQ) the TCNQ cations and TCNQ neutral molecules are arranged in face to face stacks.^{15, 16} These stacks provide, in all probability, a conducting path through the solid. If polarizable groups, such as large organic cations, indeed have the influence on conduction electrons, as was suggested by Little, then a rather obvious experiment is to surround the TCNQ stacks with such ions and see what their influence is on the conductivity. The advantages of this model are that a variety of cyanine cations can be used and that the syntheses present no real problems. For this study five simple (diethyl cyanine)⁺ TCNQ⁻ salts (i.e. no neutral TCNQ present) were prepared as well as four corresponding complex (diethyl cyanine)⁺ TCNQ⁻ TCNQ salts. It was also realized that steric factors can have a large influence on the conductivity of organic solids. An illustrative example in which steric factors may play a role, among other things, was reported by Melby¹⁷ who found that the conductivity of (N-methylphenazinium)⁺ TCNQ⁻ is about eleven orders of magnitude larger than that of (N-ethylphena-

zinium)⁺ TCNQ⁻. In view of this observation, one cyanine cation was synthesized with N-methyl groups and the conductivity of its complex TCNQ derivative was compared with that of the salt in which the cyanine cation contains N-ethyl groups. Their conductivities have essentially the same value. An X-ray diffraction pattern of the dimethyl derivative indicated the presence of stacks of parallel TCNQ entities with an interplanar spacing of about 3.3 Å. All compounds were identified by elemental analysis as well as by their absorption spectra between 200 and 1000 mμ. In acetonitrile solutions of the simple salts, the absorptions due to TCNQ⁻ at 842 and 420 mμ have an intensity ratio of about 2, while in the complex salts the ratio of the bands at 842 and 395 mμ is about 0.5¹⁸

Experimental

MATERIALS

Most diethyl cyanine dyes used as starting materials were obtained in the form of iodides from L. Light & Company, Ltd., Colnbrook, Bucks, England, while pinacyanol chloride was obtained from Fisher Scientific Company.

The purity of these compounds was checked by elemental and spectroscopic analysis. Purification prior to the conversion into the TCNQ derivatives proved unnecessary.

1,1'-Dimethyl-2,4'-cyanine iodide was prepared according to Hamer¹⁹ and then converted into the complex TCNQ derivatives as described later.

Solvents were purified by distillation: acetonitrile (from P₂O₅); dimethylcyanamid (in vacuum); tetrahydrofuran (from LiAlH₄) and n-butanol (at normal pressure).

SYNTHESES

I. (1,1'-diethyl-2,2'-cyanine)⁺ TCNQ⁻

To a boiling solution of 2.16 g of 1,1'-diethyl-2,2'-cyanine iodide in 400 ml of absolute ethanol was added a solution of 1.03 g of LiTCNQ¹⁸ in 75 ml of absolute ethanol. After 5 hr, dark purple

microcrystals were filtered off and dried in vacuum. One and four tenths grams of this material were heated to 100°C with 65 ml of n-butanol, the solution was filtered and after cooling 760 mg of green microcrystals were collected by filtration. Dried in vacuum.

Calculated for $C_{35}H_{27}N_6$: C 79.10; H 5.08; N 15.82.

Found: C 78.9; H 5.3; N 15.8.

The intensity ratio of the absorption at 842 and 420 $m\mu$ is 1.44; the deviation from 2 being due to partial overlap of cation absorption at 520 $m\mu$ and the band at 420 $m\mu$.

II. $(1,1'\text{-diethyl-2,2'\text{-cyanine}})^+ TCNQ^- .TCNQ$

Mixing solutions of equivalent amounts of I and TCNQ in dimethylcyanamide resulted in immediate precipitation of purplish-brown microcrystals. Two hundred milligrams of this material were dissolved in 20 ml of boiling acetonitrile, the solution was filtered hot and kept at room temperature for about $2\frac{1}{2}$ hr. The resulting olive-green crystals were filtered off, washed with ice-cold acetonitrile, with dry ether and dried in vacuum. Yield: 113 mg.

Calculated for $C_{47}H_{31}N_{10}$: C 76.73; H 4.22; N 19.06.

Found: C 76.8; H 4.4; N 18.7.

The intensity ratio of the absorption bands at 842 and 395 $m\mu$ is 0.51.

III. $(1,1'\text{-diethyl-2,4'\text{-cyanine}})^+ TCNQ^-$.

To a boiling solution of 1.13 g of 1,1'-diethyl-2,4'-cyanine iodide in 50 ml of methanol was added 530 mg of LiTCNQ dissolved in 50 ml of hot methanol. After the mixture had cooled to room temperature it was further cooled in an ice bath. The green, felt-like crystalline mass was then filtered, washed with cold methanol and dried in vacuum. Yield: about 1 g. The material was recrystallized from methanol.

Calculated for $C_{35}H_{27}N_6$: C 79.10; H 5.08; N 15.82.

Found: C 78.1; H 5.3; N 15.8.

The intensity ratio of the absorption bands at 842 and 420 $m\mu$ is 1.7. There is some overlap between the cation absorption at 556 $m\mu$ and the band at 420 $m\mu$.

IV. $(1,1'-diethyl-2,4'-cyanine)^+ TCNQ^- .TCNQ$

One hundred and four tenths milligrams of III and 38.7 mg of TCNQ were dissolved in 3.9 ml of boiling acetonitrile. Upon cooling solidification occurred, leaving only a small volume of liquid. After decanting the liquid the material was first washed with a mixture of acetonitrile and ether (1:1) and then with ether. Dried in vacuum. Yield: 128 mg of brownish purple powder.

Calculated for $C_{47}H_{31}N_{10}$: C 76.73; H 4.22; N 19.06.

Found: C 76.4; H 4.2; N 18.9.

The ratio of absorption intensities at 842 and 395 $m\mu$ is 0.51.

V. $(1,1'-dimethyl-2,4'-cyanine)^+ TCNQ^- .TCNQ$

Seven and two tenths grams of N-methylquinaldinium iodide and 20 g of N-methylquinolinium iodide were refluxed with 180 ml of methanol. After addition of a solution of 1.5 g of KOH in 10 ml of methanol, refluxing was continued for 25 min. The purple solution was concentrated by evaporation and then cooled. Two and four tenths grams of a purple solid were obtained which were recrystallized from a methanol-ether mixture.

One gram of this material was dissolved in 175 ml of acetonitrile, the solution was filtered and then heated to the boiling point. The hot solution was added to a hot solution of 1.0 g of TCNQ in 75 ml of acetonitrile, and the resulting mixture was left over night. A dark bronze-colored crystalline precipitate had formed; it was filtered off and recrystallized from acetonitrile. Several attempts to increase the size of the crystals were unsuccessful.

Calculated for $C_{45}H_{27}N_{10}$: C 76.38; H 3.82; N 19.80.

Found: C 75.9; H 4.7; N 19.5.

The intensity ratio of the absorptions at 842 and 395 $m\mu$ is 2. Attempts to prepare the simple salt from the cyanine iodide and

LiTCNQ always resulted in formation of the complex salt. A Debye-Scherrer powder pattern of the complex salt was obtained using CuK_α radiation. A strong line at 3.3 Å indicates the presence of stacks of parallel TCNQ molecules with a perpendicular interplanar spacing of about 3.3 Å.^{15, 16} The fact that the 3.3 Å line is broadened suggests some disorder in the TCNQ stacks. Lines corresponding to neutral TCNQ or 1,1'-dimethyl-2,4'-cyanine iodide were absent indicating that the salt contains less than 1 % of these substances.

VI. (1,1'-diethyl-4,4'-cyanine)⁺ TCNQ⁻

To a boiling solution of 1.69 g of 1,1'-diethyl-4,4'-cyanine iodide in 350 ml of absolute ethanol was added a solution of 0.80 g of LiTCNQ in 75 ml of absolute ethanol. After standing at room temperature for 4 hr bright green microcrystals were filtered off, washed with absolute ethanol and dried in vacuum. Yield: 1.81 g.

Calculated for $\text{C}_{35}\text{H}_{27}\text{N}_6$: C 79.10; H 5.08; N 15.82.

Found: C 78.9; H 5.2; N 15.6.

The ratio of absorption intensities at 842 and 420 $\text{m}\mu$ is 1.6.

VII. (1,1'-diethyl-4,4'-cyanine)⁺ TCNQ⁻ . TCNQ

One hundred and two tenths milligrams of VI and 58.8 mg of TCNQ were dissolved in 6 ml of boiling acetonitrile. Upon cooling a brownish-purple material separated out. It was filtered off, washed with ether and dried in vacuum.

Calculated for $\text{C}_{47}\text{H}_{31}\text{N}_{10}$: C 76.73; H 4.22; N 19.06.

Found: C 76.4; H 3.6; N 19.4.

The intensity ratio between the 842 and the 395 $\text{m}\mu$ absorption bands is 0.44.

VIII. (1,1'-diethyl-2,2'-carbocyanine)⁺ TCNQ⁻

To a boiling solution of 2.16 g of pinacyanolchloride in 500 ml of absolute ethanol was added a solution of 1.17 g of LiTCNQ in 150

ml of absolute ethanol. After standing for 6 hr, dark green microcrystals were filtered, washed with small portions of cold ethanol and then with ether. Dried in vacuum. Yield: 1.97 g.

Calculated for $C_{37}H_{29}N_6$: C 79.71; H 5.21; N 15.08.

Found: C 79.4; H 5.6; N 14.8.

The ratio of absorption intensities at 842 and 420 $m\mu$ is about 1.5.

IX. $(1,1'\text{-diethyl-2,2'\text{-carbocyanine}})^+ TCNQ^- .TCNQ$

To a hot solution of 0.32 g of TCNQ in dry tetrahydrofuran was added 0.26 g of VIII. Dark brown microcrystals separated from the dark green solution before cooling to room temperature. The warm mixture was filtered and the crystals were washed with absolute ethanol and with ether. Dried in vacuum. Yield: almost quantitative. The sample was recrystallized twice from acetonitrile (about 10 mg/ml).

Calculated for $C_{49}H_{33}N_{10}$: C 77.26; H 4.34; N 18.39.

Found: C 77.4; H 4.5; N 18.7.

The ratio of absorption intensities at 842 and 395 $m\mu$ is 0.51.

X. $(1,1'\text{-diethyl-4,4'\text{-carbocyanine}})^+ TCNQ^-$

To a boiling solution of 1.68 g of 1,1'-diethyl-4,4'-carbocyanine iodide in 550 ml of absolute ethanol was added a solution of 0.74 g of LiTCNQ in 60 ml of absolute ethanol. After standing for 6 hr bright green microcrystals were filtered, washed with cold ethanol and dried in vacuum. Yield: 1.55 g.

Calculated for $C_{37}H_{29}N_6$: C 79.71; H 5.21; N 15.08.

Found: C 79.8; H 5.3; N 14.8.

The intensity ratio of the absorption intensities at 842 and 420 $m\mu$ is about 1.3.

Efforts to prepare the corresponding complex TCNQ salt were unsuccessful.

ELECTRICAL MEASUREMENTS

Due to the fact that all the compounds listed were obtained in the form of brittle microcrystals, it was not feasible to measure the conductivity on single crystals. Instead, an estimate of the conductivity was obtained by measurements on compactions. Contacts were established by using a gallium-indium alloy. The results are given in Table 1.

TABLE 1 Conductivity of Cyanine-TCNQ Compounds

Sample	σ (300°K) ($\Omega^{-1}\text{cm}^{-1}$)
I. (1,1'-diethyl-2,2'-cyanine) ⁺ TCNQ ⁻	1.0×10^{-9}
II. (1,1'-diethyl-2,2'-cyanine) ⁺ (TCNQ) ₂ ⁻	2.5×10^{-3}
III. (1,1'-diethyl-2,4'-cyanine) ⁺ TCNQ ⁻	7.0×10^{-7}
IV. (1,1'-diethyl-2,4'-cyanine) ⁺ (TCNQ) ₂ ⁻	1.3×10^{-4}
V. (1,1'-dimethyl-2,4'-cyanine) ⁺ (TCNQ) ₂ ⁻	1.5×10^{-4a}
VI. (1,1'-diethyl-4,4'-cyanine) ⁺ TCNQ ⁻	7.0×10^{-8}
VII. (1,1'-diethyl-4,4'-cyanine) ⁺ (TCNQ) ₂ ⁻	4.0×10^{-4}
VIII. (1,1'-diethyl-2,2'-carbocyanine) ⁺ TCNQ ⁻	6.0×10^{-10}
IX. (1,1'-diethyl-2,2'-carbocyanine) ⁺ (TCNQ) ₂ ⁻	1.8×10^{-5}
X. (1,1'-diethyl-4,4'-carbocyanine) ⁺ TCNQ ⁻	8.0×10^{-11}

^a Measured on a four point-probe sample. At 77°K the conductivity has decreased to about $10^{-8} \Omega^{-1}\text{cm}^{-1}$.

Discussion

As is illustrated by the results in Table 1, the materials studied do not seem to have any potential as room temperature superconductors. In fact, these results fall within the range of conductivities reported for other TCNQ derivatives.¹⁸

If the polarizability of the positive ion would be responsible for enhancing the conductivity, one would expect a compound like VIII ((1,1'-diethyl-2,2'-carbocyanine)⁺ (TCNQ)₂⁻) to have a higher conductivity than (1,1'-diethyl-2,2'-cyanine)⁺ (TCNQ)₂⁻ (II) because the carbocyanine is more polarizable than the simple cyanine. However, it turns out that the conductivity of the cyanine is 100

times larger than that of the carbocyanine. In general, it seems that, by going to larger cyanine ions, the conductivity decreases for the simple TCNQ^- salts as well as for the complex $(\text{TCNQ})_2^-$ salts. In addition to the polarizability of the cations, steric factors could play a decisive role. Discussion of this aspect has to be postponed until more detailed information concerning the crystal structure becomes available.

The information presented here clearly indicates that these compounds do not represent good models for organic superconductors. They are certainly not of the precise type suggested by Little, but represent an attempt at experimental verification of his concept. It is clear that both experimentally and theoretically the idea of organic superconductors needs further examination.

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