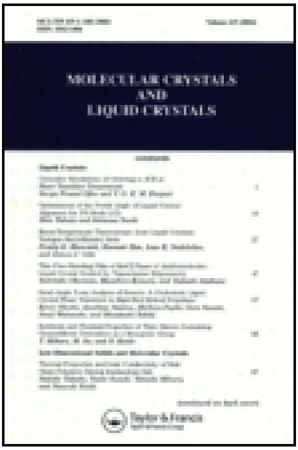

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

BIPA $(TCNQ)_2$, A New Highly Conducting TCNQ Salt

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Version of record first published: 20 Apr 2011.

To cite this article: H. Strzelecka , J. Rivory & S. Flandrois (1981): BIPA $(TCNQ)_2$, A New Highly Conducting TCNQ Salt, Molecular Crystals and Liquid Crystals, 69:3-4, 167-172

To link to this article: http://dx.doi.org/10.1080/00268948108072697

Mol. Cryst. Liq. Cryst., 1981, Vol. 69, pp. 167–172
0026-8941/81/6903-0167/$06.50/0

BIPA $(TCNQ)_2$, A New Highly Conducting TCNQ Salt

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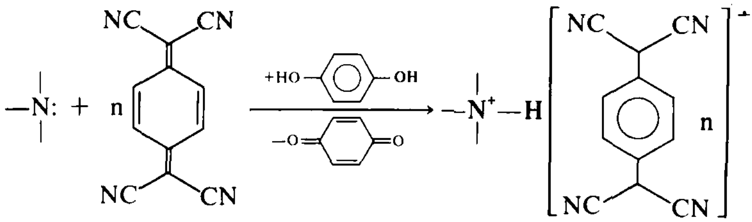
(*Received August 5, 1980; in final form September 29, 1980*)

Protonated 2,2'-Bipyridylamine—TCNQ 1: 2 salt: BIPA $(TCNQ)_2$ was synthetized via a redox process. Its metallic character is shown through electrical, optical and magnetic susceptibility measurements.

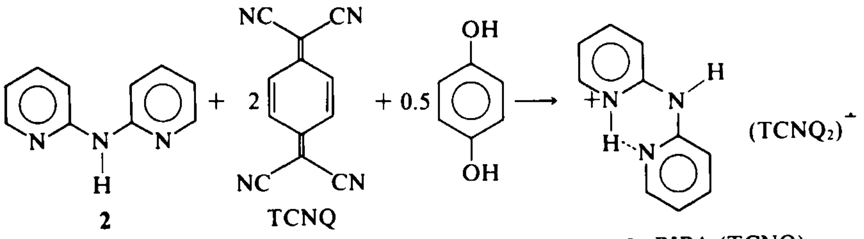
In order to understand the relationship between molecular structure of heterocyclic amines and properties of the resulting salts, we studied the reaction:



1

We obtained some new radical salts **1** having metallic behavior.[1,2] We have shown that the conducting salts **1** are either kinetic products[3] or thermodynamic ones. For example, the salt formed from 1,10 phenanthroline, the conjugated acid of which forms a hydrogen bond, is found to be thermodynamically stable product.

In order to verify if the ability of the cation to form an intramolecular hydrogen bond may influence the stability of the radical salt, we performed the following reaction:



We choose amine **2** because its protonation leads to an ammonium cation having an intramolecular hydrogen bond.[4]

We report here the synthesis and physical properties of the new salt 3: BIPA$(TCNQ)_2$.

SYNTHESIS

Commercial (Aldrich) 2-pyridinamine, N-2 pyridinyl, **2**, was purified by crystallization from water. TCNQ (Aldrich) was purified by extraction by ethyl acetate.

BIPA $(TCNQ)_2$: 3

A mixture of 171 mg (1 mmole) of amine **2**, 408 mg (2 mmoles) of TCNQ, 55 mg (0,5 mmole) of hydroquinone and 200 ml of acetonitrile was refluxed for 0.5 hr. After cooling to 20° C the black microcrystals were collected, washed with ether and dried. The yield was 550 mg (95%).

Single Crystals with typical dimensions $2 \times 0.025 \times 0.01$ mm^3 were obtained by slow cooling of an acetonitrile solution (70° C $\xrightarrow[0.3°/hr]{}$ 40° C).

The thermodynamical stability of BIPA $(TCNQ)_2$ was studied in solid state and in solution.

After heating at 100° C during 48 hr the crystalline product remains unchanged. At 200° C, we observe sublimation without decomposition. In acetonitrile solution (20° < *t* < 80°) no degradation was observed after several days.

PHYSICAL PROPERTIES

1 Electrical conductivity

Four probe d-c conductivity measurements on single crystals of BIPA $(TCNQ)_2$ mounted with platinum paint gave a room temperature value of ca 170 $(\Omega\ cm)^{-1}$.

The thermal variation of conductivity is presented in Figure 1. No hysteresis was found after cooling at 100 K.

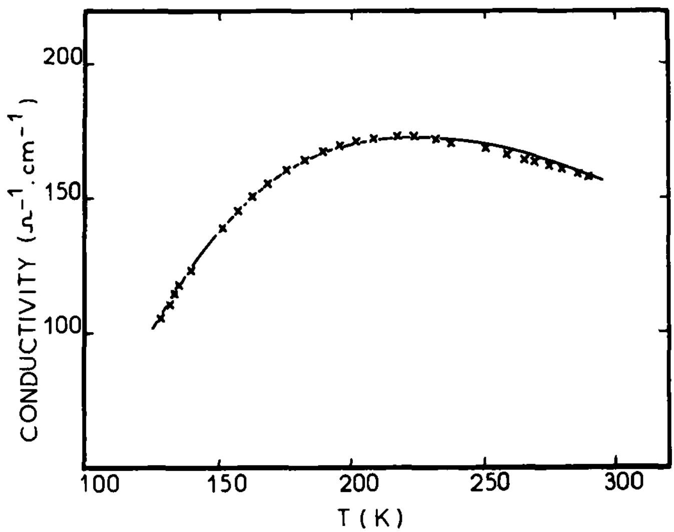


FIGURE 1 Thermal variations of conductivity of BIPA $(TCNQ)_2$ —— on heating; XXXX on cooling.

2 Optical properties

2.1 Optical absorption Figure 2 shows the optical absorption of BIPA $(TCNQ)_2$ pressed with KBr. The spectrum is characteristic of conducting 1 : 2 TCNQ salts. The minimum around 0.8 eV is related to the metallic behavior of the salt. The four peaks at 1.3, 1.46, 2.3 and 3.4 eV are related to intermolecular and intramolecular absorptions of TCNQ.[5,6]

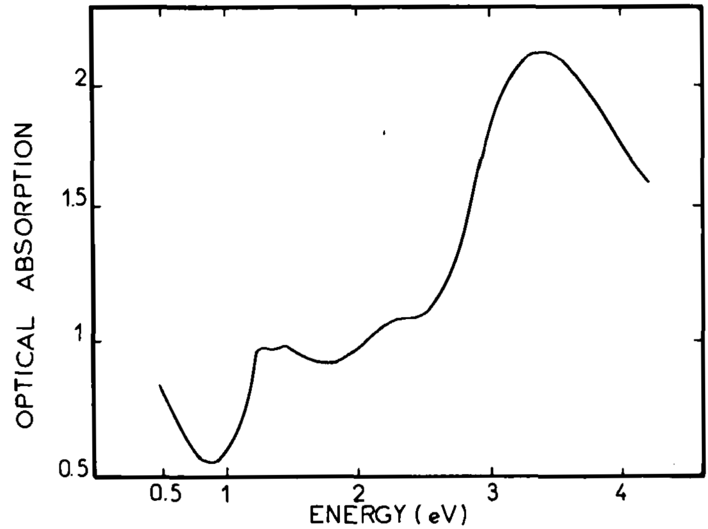


FIGURE 2 Powder absorption spectrum of BIPA $(TCNQ)_2$.

2.2 Reflectivity measurements On Figure 3, we have reported the reflectivity of a polycrystalline compaction of BIPA $(TCNQ)_2$. A steep decrease of the reflectivity is observed between 0.05 and 0.75 eV with a minimum around 0.75 eV, the position of which is related to the plasma frequency. In order to fit these results, we use for the dielectric function an expression containing a

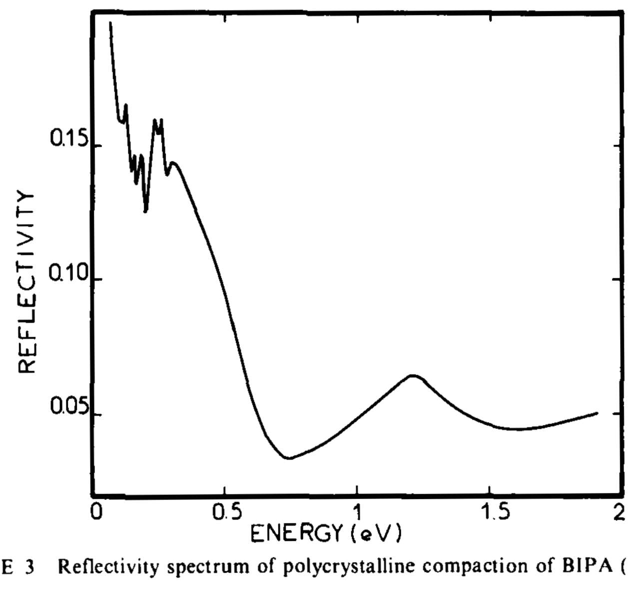


FIGURE 3 Reflectivity spectrum of polycrystalline compaction of BIPA $(TCNQ)_2$.

Drude term and an oscillator term which accounts for the maximum observed around 1.4 eV:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} - \frac{s}{\omega^2 - \omega_1^2 + i\gamma\omega}$$

ω_p is the plasma frequency, τ the relaxation time; s, ω_1, γ are respectively the strength, the frequency and the damping of the oscillator.

We found:	$\epsilon_\infty = 2.01$	$\omega p = 1.2$ eV	$h/\tau = 0.37$ eV
	$s = 1.2$	$\omega_1 = 1.14$ eV	$\gamma = 0.4$ eV

No attempt has been done to account for a variation of the relaxation time. The optical conductivity at zero frequency: $\omega_p^2\tau/4\pi$ is equal to 530 $(\Omega\ \text{cm})^{-1}$ which is higher than the measured d-c conductivity value, as observed in many cases for materials having a d-c conductivity ratio σ_{Max}/σ_{RT} nearby 1. For such materials with "metal-like" behavior, an alternative model has been proposed which postulates a semi-conducting state at all temperatures.[7]

3 Magnetic properties

The magnetic susceptibility was measured with a Faraday balance. The paramagnetism was obtained by subtracting the core diamagnetism calculated from Pascal constants. The results are shown in Figure 4. The paramagnetic susceptibility has a room temperature value close to 6×10^{-4} emu/mole, is almost temperature independent down to 50 K and increases sharply at lower temperatures. This behavior is typical of conducting TCNQ salts with 1:2 stoichiometry.

It has been shown,[8] that at low temperatures the susceptibility of these salts do not obey a Curie law characteristic of non-interacting paramagnetic centres, but instead the law:

$$\chi = AT^{-\alpha}$$

is obeyed, with α less than unity. Indeed, for BIPA $(TCNQ)_2$ this law is obeyed at low temperatures with $\alpha \sim 0.8$ and $A \sim 50 \times 10^{-4}$ emu/mole/$K^{0.8}$. The result obtained by subtracting this contribution is shown in Figure 4 (crosses). A break in the curve appears around 15K, which could be evidence for a phase transition.

CONCLUSION

We have synthetized BIPA $(TCNQ)_2$ a new high conducting ($\sigma_{RT} = 170\ \Omega^{-1}\ \text{cm}^{-1}$) unusually stable TCNQ salt. The thermal stability was at-

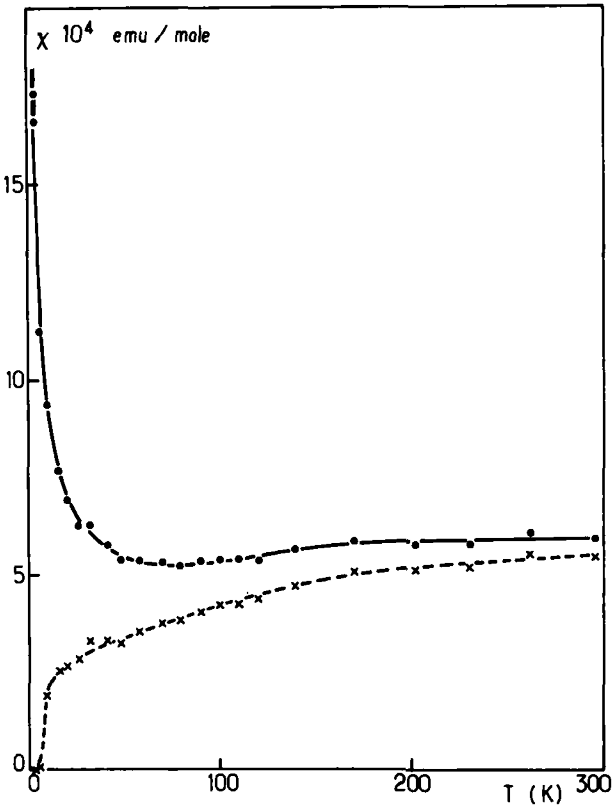


FIGURE 4 Temperature dependence of the paramagnetic susceptibility of BIPA $(TCNQ)_2$

. . . . $\chi_p = \chi_{meas.} - \chi_{core}$
x x x x $(\chi_p - AT^{-\alpha})$

tributed to the presence of an intramolecular hydrogen bond. Its conducting character was shown through electrical, optical and magnetic susceptibility measurements.

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