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

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Version of record first published: 17 Oct 2011.

To cite this article: J. Amzil , M. Brutus , J. M. Catel , G. LE Coustumer , Y. Mollier & M. Stavaux (1985): Organic conductors: TCNQ ion Radical Salts with Alkylchalcooenouronium and 1. 2-Dithioliuw Cations, Molecular Crystals and Liquid Crystals, 120:1, 357-360

To link to this article: http://dx.doi.org/10.1080/00268948508075819

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 357-360
0026-8941/85/1204-0357/$10.00/0

Printed in the United States of America

ORGANIC CONDUCTORS : TCNQ ION RADICAL SALTS WITH ALKYLCHALCOGENOURONIUM AND 1,2-DITHIOLIUM CATIONS

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Abstract Some complex ion radical salts of TCNQ with S and Se-alkylchalcogenouronium cations and 1,2-dithiolium cations were prepared. The optical spectra determined by diffuse reflectance and absorption show four bands for all conducting salts. Electrical conductivity of compacted powders are measured at room temperature and for some salts on single crystals.

In the field of anion radical salts of TCNQ with organic cations, we have prepared some new materials[1,2] including alkylthiouronium, alkylselenouronium and 1,2-dithiolium as counter ions. Tables I and II show the ion radical salts with 1/2 and 2/3 stoichiometries and their electrical conductivities on powders.

OPTICAL PROPERTIES

The solid state absorption spectra were measured on powders in compressed KBr pellets, between 40000 cm^{-1} and 200 cm^{-1} by diffuse reflectance in the UV and near IR range by transmission in the IR region, according to[3]. All spectra show the three bands labelled B, C and D by other authors[4]. The D band in the range 26000-27000 cm^{-1} can be attributed to TCNQ. For salts 3 we also observe in this region the absorption of the 1,2-dithiolium cation. The C band at about 16000 cm^{-1} is generally

attributed to the presence of the dimer $(TCNQ^-)_2$ [5]. At low energies the peak appearing near 10500 cm^{-1} and noted B or CT_1 band[6] has been assigned to transition between $TCNQ^{\cdot-}$ radical anions[4]. However for 1/2 salts exhibiting a relatively high conductivity this absorption would be due to intramolecular transitions of $TCNQ^{\cdot-}$ [5 6 7].

For all conducting salts 1 and 3 [$\sigma \geq 0,1$ $(\Omega cm)^{-1}$] the absorption decreases to a minimum near 8000 cm^{-1} corresponding roughly to the plasma frequency. For 1e, the plasma frequency defined from specular reflectance curves is 6860 cm^{-1} [8]. In the IR region, the optical density increases with decreasing energy to a peak centered at about 3000 cm^{-1}. This peak labelled A [4] or or CT_2 [6] is found in all organic conducting salts. We can notice that 1e which exhibits such a peak at 3000 cm^{-1} has a single crystal conductivity of 70 $(\Omega cm)^{-1}$ along the stack axis at room temperature [8].

ELECTRICAL CONDUCTIVITIES

The electrical conductivities of ions radical salts 1 are dependent of the substituent on the chalcogen. Thus the conductivity is about 10^3 times higher with a S-ethyl than with a S-methyl ; but a new lengthening of the S-alkyl chain decreases the conductivity. In the N,N,N',N'-tetramethylchalcogenouronium salts any significant change of conductivity is observed with change in the chalcogen atom. The influence of substituents on the conductivities of ions radical salts 3 is less typical. However we notice an increasing of conductivity upon replacing aliphatic substituents by groups including available π electrons.

Some single crystals of ions radical salts have been obtained and their electrical conductivities along stack axis measured :

1e $\sigma_{RT} = 70 (\Omega cm)^{-1}$ [8] 1i $\sigma_{RT} = 20 (\Omega cm)^{-1}$ [8]

3d $\sigma_{RT} = 4 (\Omega cm)^{-1}$

The crystal structure of 5-t-butyl-3-methylthio-1,2 dithiolium $(TCNQ)_2$ is quite similar to the one found in another complex salt TMPD $(TCNQ)_2$ [9]. There are segregated stacks of TCNQ and cations, the latter being inclined at an angle of 40° to the stack axis. Mean spacing between TCNQ units is 3,24 Å and TCNQ stacks have a zig-zag arrangement. Electrical resistivity measurements of this salt as function of temperature in the 120 to 284 K range show a semiconducting behaviour with an energy gap of 0,18 eV, similar to the one of TMPD $(TCNQ)_2$ [10].

TABLE I Conductivities of TCNQ ions radical salts with chalcogenouronium cations.

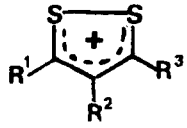
1 x/y = 1/2

2 x/y = 2/3

Ref.	X	R	R'	R''	σ $(\Omega cm)^{-1}$
1a	S	CH_3	CH_3	H	4×10^{-2}
1b	S	CH_3	CH_3	CH_3	3.2×10^{-4}
*1c	S	CH_3	CH_2-	H	8×10^{-3}
1d	S	C_2H_5	CH_3	H	0.13
1e	S	C_2H_5	CH_3	CH_3	0.35
1f	S	n-C_3H_7	CH_3	CH_3	5×10^{-3}
1g	S	n-C_4H_9	CH_3	CH_3	4×10^{-2}
1h	Se	CH_3	CH_3	CH_3	3.7×10^{-4}
1i	Se	C_2H_5	CH_3	CH_3	0.22
2a	S	CH_3	C_2H_5	H	5.5×10^{-4}
2b	S	C_2H_5	C_2H_5	H	2×10^{-5}

* 1c : S-Methyl N,N'ethylenethiouronium cation

TABLE II Conductivities of TCNQ ions radical salts with 1,2-dithiolium cations stoichiometry 1/2



$TCNQ_2^{\cdot -}$ 3

Ref.	R^1	R^2	R^3	σ $(\Omega cm)^{-1}$
3a	C_6H_5	H	H	0.4
3b	H	C_6H_5	H	0.6
3c	C_6H_5	H	SCH_3	0.75
3d	$(CH_3)_3C$	H	SCH_3	8×10^{-2}
3e	H	CH_3	SCH_3	7×10^{-3}
3f	C_6H_5	H	C_6H_5	0.37
3g	p-CH_3O-C_6H_4	H	p-CH_3O-C_6H_4	5×10^{-2}
3h	CH_3	H	CH_3	8×10^{-3}
3i	CH_3S	CH_3S	CH_3S	0.4
3j	CH_3S	C_6H_5	CH_3S	4×10^{-3}

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