This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 20 February 2013, At: 12:38

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH,

UK



Molecular Crystals and Liquid Crystals

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

Electric and Magnetic Properties of 4, 4', 5, 5'-Tetramethoxy-2, 2'-Dithiobiphenyl lodide(6/7) - A New Radical Cation Salt Containing Polyiodide Chains

K. Stender $^{\rm a}$, G. Klar $^{\rm a}$, M. Peo $^{\rm a}$, W. Bauhofer $^{\rm b}$ & S. Roth $^{\rm b}$

^a Inst. f. Anorganische und Angewandte Chemie der Universität Martin-Luther-King-Platz, 3, D-2000, Hamburg, 13, Germany

^b Max-Planck-Institut für Festkörperforschung, 7, Stuttgart, 80

Version of record first published: 17 Oct 2011.

To cite this article: K. Stender , G. Klar , M. Peo , W. Bauhofer & S. Roth (1985): Electric and Magnetic Properties of 4, 4′, 5, 5′-Tetramethoxy-2, 2′-Dithiobiphenyl Iodide(6/7) - A New Radical Cation Salt Containing Polyiodide Chains, Molecular Crystals and Liquid Crystals, 120:1, 277-280

To link to this article: http://dx.doi.org/10.1080/00268948508075802

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 277-280 0026-8941/85/1204-0277/\$10.00/0
© 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd. Printed in the United States of America

ELECTRIC AND MAGNETIC PROPERTIES OF 4,4,5,5,-TETRAMETHOXY-2,2,-DITHIOBIPHENYL IODIDE(6/7) - A NEW RADICAL CATION SALT CONTAINING POLYIODIDE CHAINS

K. STENDER*, G. KLAR*, M. PEO, W. BAUHOFER, S. ROTH *Inst. f. Anorganische und Angewandte Chemie der Universität Martin-Luther-King-Platz 3, D-2000 Hamburg 13, Germany Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 80

Abstract The title compound is an example of a columnar structure formed by partially oxydized non-planar molecules, revealing the character of a p-type semiconductor with a metal-insulator transition at 260 K. Although having sulfur as hetero atoms in the molecule the conductivity must be attributed to contacts of the aryl rings.

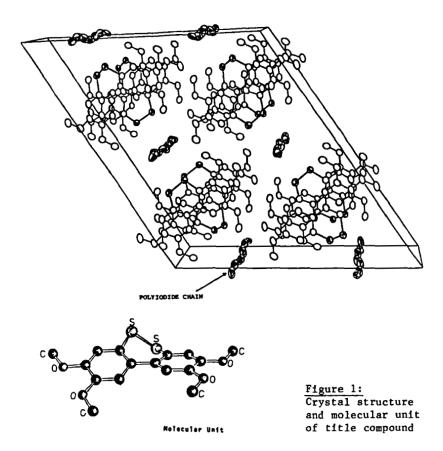
INTRODUCTION

2,3,7,8-tetramethoxythiantren (TMT), a 1,4-dithiin system, forms with iodine in acetonitril the well defined $[TMT]^{+}I_{3}^{-}$ (to be published elsewhere). In this work we are interested on the reactions of the analogous 1,2-dithiin, i.e. 4,4',5,5'-tetramethoxy-2,2'-dithiobiphenyl (DTB). In contrast to TMT, DTB reacts with iodine leading to the non-stoichiometric compound (DTB)I₁ 17, $\frac{1}{1}$.

EXPERIMENTAL

DTB was prepared from 4,4′,5,5′-tetramethoxybiphenyl and sulfur monochloride in acetic acid yielding a blue oxidation product, which can be reduced to DTB (besides DTB-oxide) by a methanolic solution of tin(II)-chloride. Needle-like single crystals of $\frac{1}{3-6mm} \times 0.15mm \times 0.15mm$ were obtained by combining solutions of DTB and iodine in acetonitril.

 $\underline{1}$ crystallizes in the monoclinic space group C2/c (Figure 1); the non-planar DTB-units (angle between planes of aryl rings 25°) are parallel stacked in b-direction, neighbouring molecules are rotated 180° around the biphenyl axis (AB-stacking). In this way all aryl rings are coplanarly arranged. The interplanar stacking distance of 349 pm is less than the sum of the Van-der-Waals radii. Polyiodide chains are disordered between the stacks and - according to Raman scattering - consist of $\rm I_5^-$ -units. The charge transfers is probably due to iodine-sulfur contacts.



ELECTRICAL CONDUCTIVITY AND OPTICAL REFLECTIVITY

The DC-conductivity, obtained by a four probe method, is shown in Figure 2. Between 270 K and 360 K the DC-conductivity along the needle axis is almost constant and in the order of 5 S/cm. Above 360 K the conductivity drops irreversibly due to evaporation of iodine. Below 270 K the conductivity falls several orders of magnitude. Thermoelectric power measurements show that the conductivity is p-type with a Seebeck coefficient of 50 mV/K.

The optical reflectivity of a single crystal was examined at room temperature between 1.4 eV and 2.4 eV. Figure 3 represents the reflectivity of linearly polarized light parallel (R#) and perpendicular (RL) to the needle axis, indicating a pronounced anisotropy of the conductivity.

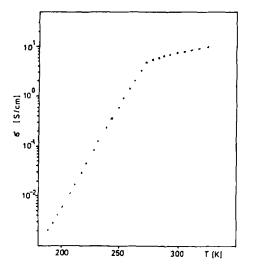


Figure 2: Single crystal DC-conductivity of title compound

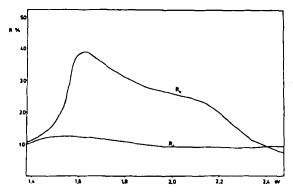


Figure 3:
Reflectivity of
linear polarized
light of the
title compound
(Serpent boa
digerant un éléphant; selon A.de
Saint-Exupéry)

MAGNETISM

The single crystals exhibit a strong Lorentzian line in th ESR signal with a line width of 0.27 mT and a g-value of 2.0059 at room temperature. The linewidth decreases with decreasing temperature down to 4 K. A sharp drop in the linewidth occurs near 270 K, the same region where the conductivity drop has been found (Figure 4). The static susceptibility was measured with a commercial SQUID magnetometer. The constant diamagnetic contribution has been substracted following Pascal's additivity rule (d = $-2.66 \cdot 10^{-4}$ emu CGS for a (DTB)I_{1·17} molecule). The susceptibility does not follow

a Curie law. There is a pronounced magnetic anomaly at $10~\mathrm{K}$ and perhaps a weak anomaly at $270~\mathrm{K}$ (Fig. 5), correlated to the drop in the conductivity (Fig. 2) and in the ESR linewidth (Fig. 4). The number of localized spins ist calculated from the Curie constant, assuming g=2 and s=1/2 and amounts to $1.4 \cdot 10^{23}~\mathrm{spin/mole}$).

We want to thank the Stiftung Volkswagenwerk for financial support.

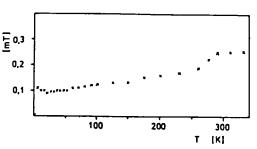


Figure 4: ESR-linewidth of the title compound

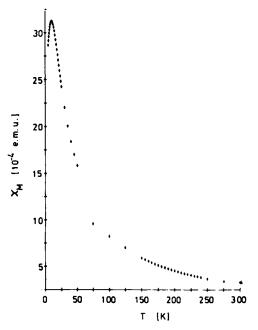


Figure 5: Static susceptibility of the title compound