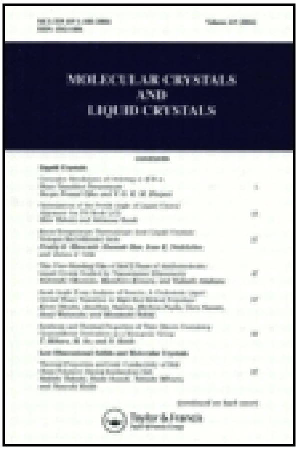

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Electric and Magnetic Properties of 4, 4′, 5, 5′-Tetramethoxy-2, 2′-Dithiobiphenyl Iodide(6/7) - A New Radical Cation Salt Containing Polyiodide Chains

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

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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.

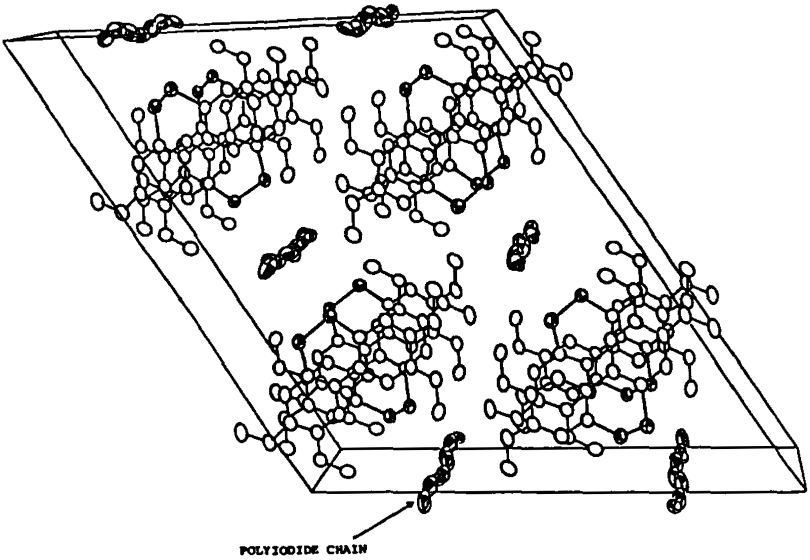
INTRODUCTION

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 $(DTB)I_{1\ 17}$, 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 1 (3-6mm x 0.15mm x 0.15mm) were obtained by combining solutions of DTB and iodine in acetonitril.

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 I_5^{-}-units. The charge transfers is probably due to iodine-sulfur contacts.



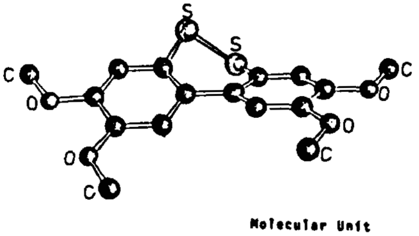


Figure 1:
Crystal structure
and molecular unit
of title compound

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 ($R_{\parallel}$) and perpendicular ($R_{\perp}$) to the needle axis, indicating a pronounced anisotropy of the conductivity.

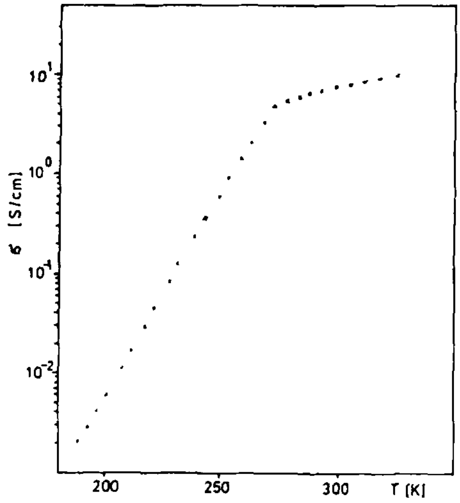


Figure 2:
Single crystal DC-conductivity of title compound

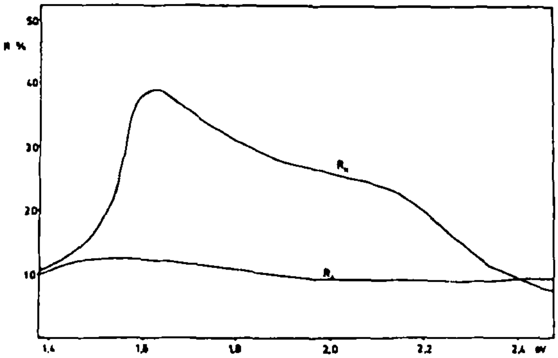


Figure 3:
Reflectivity of linear polarized light of the title compound (Serpent boa digerant un éléphant; selon A.de Saint-Exupéry)

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 K and perhaps a weak anomaly at 270 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 $1.4 \cdot 10^{23}$ spin/mole).

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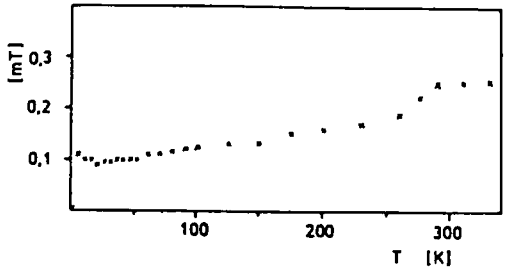

Figure 4:
ESR-linewidth of
the title compound

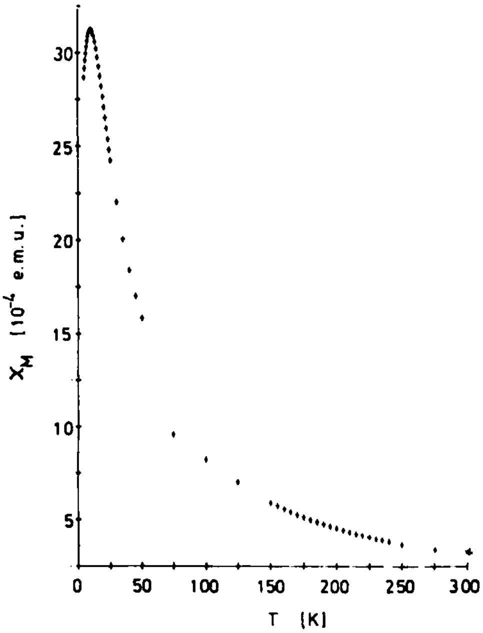

Figure 5:
Static susceptibility
of the title compound