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Role of heteroatoms in the design and synthesis of organic metals

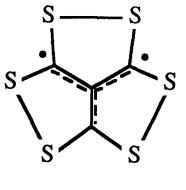
Fred Wudl, Gordana Srdanov, Bernhard Rosenau, Daniel Wellman, Keith Williams, Sherman D. Cox and Valentine Yoon

Institute for Polymers and Organic Solids, Departments of Physics and Chemistry, University of California, Santa Barbara, CA 93106

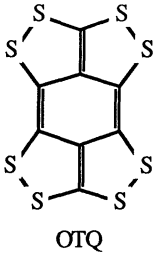
Abstract - Strategies for the syntheses of two new donors based on chalcogens are presented. The successful synthesis and determination of physical properties of Δ-2-1,3-dithiole (Δ-4-3,5-dithiono-1,2 dithiole, **4**) and conversion routes from this unusual heterocycle to dithiolodithiole (DTDT, **3**) and octathioquinodimethane (OTQ, **2**) are presented. Evidence for the conversion plus some physical properties are discussed.

INTRODUCTION

Several years ago we proposed the development of organic ferromagnets based on sulfur heterocycles possessing D_{3h} symmetry (**1**) (ref. 1) and the design of new acceptors based on annulated sulfur heterocycles of D_{2h} symmetry (**2**) (ref. 2). Furthermore, it was speculated that the latter could be prepared from the former. The molecules we proposed are shown below.

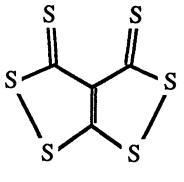


HTTM
1

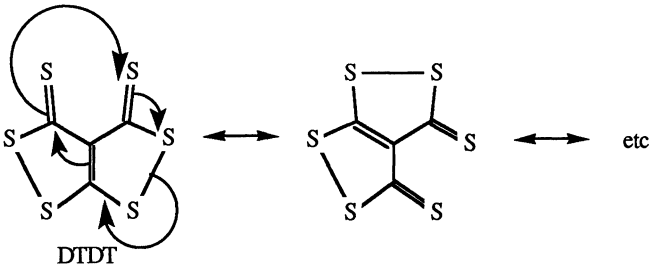


OTQ
2

In this report we will focus on the synthesis of a precursor to **1**, the theoretically interesting dithiolodithiole **3**. The theoretical aspects of **3** have been considered by Gleiter (ref. 3), particularly in regard to its automerization:



DTDT
3

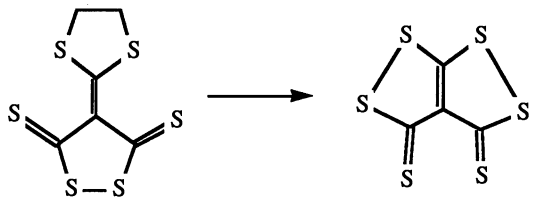


DTDT

Since our original proposal of **1** as a precursor of ferromagnetic organic metals (FOM), a recent calculation revealed that in fact (**1**) may turn out to produce ferrimagnetic solids (ref. 4).

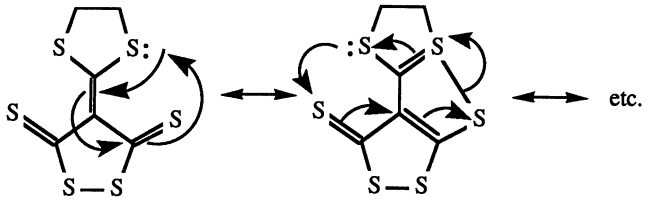
RESULTS AND DISCUSSION

The synthesis of **3** was possible in one step by the pyrolysis of compound **4**:



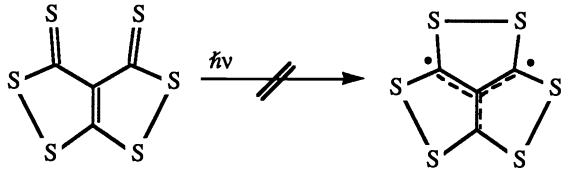
4

Compound (**4**) is interesting on its own right because in its X-ray crystallographically determined structure it exhibits bond lengths which are more consistent with resonance contributors such as **4a**:



4 **4a**

because all the double bonds are considerably longer than expected and the single bonds to sulfur are shorter than expected, also the non-bonded sulfur atoms show an intramolecular interatomic distance of 2.95 Å which is 0.65 Å shorter than the sum of the Van der Waals radii of sulfur.
Both compounds **4** and **3** are deeply colored and the longest absorption peak is displaced toward the red in the solids as compared to solutions.
Compound **3**, contrary to our expectations, does not show a photoinduced ESR signal either in solution at room temperature or in the frozen matrix:



So far we have not been able to find a solvent in which **3** is soluble over a wide temperature range to determine if it automerizes and if so what the activation parameters are.

REFERENCES

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