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PREPARATION, PURIFICATION, AND POLYMORPHISM OF TETRASELENOTETRACENE (TSeT)

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ABSTRACT

The preparation and characterization of high purity samples of tetraselenotetracene (TSeT) free of tetrathiotetracene are described. A new monoclinic phase of TSeT, $\underline{a} = 15.70$, $\underline{b} = 4.093$, $\underline{c} = 11.47$Å, $\underline{\beta} = 92.9°$, V = 736.7Å^3, Z = 2, space group $P2_1/n$, was isolated by slow cooling of a chlorobenzene solution.

INTRODUCTION

Pursuant to our continuing interest in dichalcogenide derivatives of the aromatic hydrocarbons (2) as well as general interest in pi-donors of the heavier chalcogens as precursors to low temperature organic metals (3), we noted that tetrathiotetracene (TTT) (4) and other chalcogen derivatives of tetracene (5) exhibited a lattice constant of ca. 4Å. Since the reported (6) crystal structure of tetraselenotetracene (TSeT,**1**) carried out on crystals grown by sublimation lacks such a lattice constant, we crystallized TSeT from solution and quickly noted from the X-ray powder pattern the existence of a new phase.

In addition to the report of polymorphism in TSeT, this paper also describes the most detailed preparation and purification reported to date.

EXPERIMENTAL

Diffuse reflectance and solution absorption spectra were recorded on a Cary 17D spectrophotometer. Samples for diffuse reflectance were 1% dispersions in either LiF or

NaCl. Infrared spectra were recorded on a Nicolet Fourier Transform spectrophotometer. Differential scanning calorimetry was performed on a DuPont 1090 instrument in nitrogen atmosphere at a heating rate of twenty degrees per minute.

Preparation of 5,11-Dichlorotetracene

This compound was synthesized as previously described.(7) The crude product was exhaustively washed with saturated sodium sulfide solution followed by column chromatography in benzene solution on silica gel. Comparison of the material before and after chromatography by thin layer chromatography reveals the removal of at least three tetracene derivatives in the purified material. Our samples exhibit m.p. 227° (lit(7) m.p. 220°). Occasionally, trichlorotetracene was detected in our samples by mass spectrometry.

Preparation and Purification of TSeT

TSeT was synthesized from 5,11-dichlorotetracene, prepared as above, and selenium as described by Goodings, et al.(7) The dark solid isolated from the reaction mixture was washed with saturated sodium sulfide solution until the washings were colorless, water, and ethanol, followed by vacuum drying. Further purification was accomplished by gradient sublimation on Kapton at 300° and 2-5 x 10^{-7}mm. Differential scanning calorimetry of our best samples reveals the absence of elemental selenium, readily detectible in less pure samples, and decomposition at 410°. The absorption spectrum of TSeT in 1,2,4-trichlorobenzene exhibits the following λ_{max}: 714 (log ε 4.13), 655 (3.99), 468 nm (3.93), in good agreement with a previous report.(8)

Anal. Calcd for $C_{18}H_8Se_4$: C, 40.03; H, 1.49; Se, 58.48. Found: C, 39.80; H, 1.69.

RESULTS AND DISCUSSION

We have noted several indications that TSeT prepared as described herein is of superior quality versus several other reports in the literature. We regard the removal of sulfur from 5,11-dichlorotetracene as critical, since sulfur is known(9) to react with this compound to give TTT. Compacted samples of our gradient sublimed TSeT exhibit a resistivity of 10^8 ohm-cm, more insulating than reported in other work.(7,10) Additionally, our samples of TSeT are less soluble in dimethylformamide than others(11) used to make $(TSeT)_2^+Cl^-$.

When a chlorobenzene solution of gradient sublimed TSeT was slowly cooled, a greenish-black crystalline solid, whose X-ray powder pattern was markedly different than that of the sublimed TSeT was obtained. Weissenberg and Burger precession photographs of single crystals of TSeT from chlorobenzene revealed the existence of a new monoclinic phase: $\underline{a}$ = 15.70, $\underline{b}$ = 4.093, $\underline{c}$ = 11.47Å, β = 92.9°, V = 736.7Å^3, Z = 2, space group $P2_1/n$. This crystal is isomorphous to the phase of tetratellurotetracene (TTeT) we have structurally characterized.(1,5)

Careful analysis of our X-ray powder patterns of both sublimed and solution grown TSeT vis-a-vis calculated patterns of both the previously known(6) orthorhombic phase and the new monoclinic phase revealed that all of our experimental samples were mixtures of the two phases with the orthorhombic being the major component of the sublimed material and the monoclinic as the major portion of the solution grown crystals. While polymorphic solids often exhibit differences in physical properties, we did not observe any significant differences in the solid state infrared spectra of either sublimed or solution grown TSeT in the 4000-200 cm^{-1} range. The diffuse reflectance of either sublimed or solution grown TSeT was not significantly different and exhibited maxima in the remission function at 755,640, and 470 nm. We note that the low energy maximum is red shifted versus the solution spectrum noted above.

In summary, we have described modifications of existing methodology to prepare TSeT free of TTT, and we find differential scanning calorimetry a convenient technique for monitoring purity. A new polymorph of TSeT with a linear chain crystal structure has been identified.

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