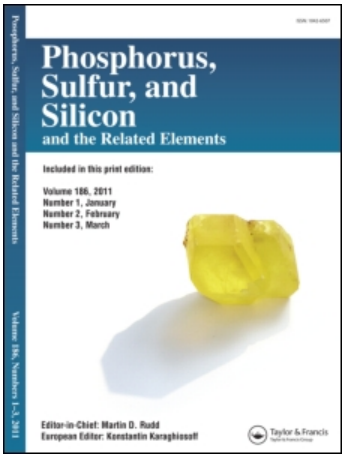

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESES AND CHARACTERIZATION OF 1,3-DITHIEPIN-2-CARBODITHIOLATE AND ITS ALKYLATED DERIVATIVES

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To cite this Article Long II, Carl J. , Naylor, Mark , Moreland, Charles , Bordner, Jon and Bereman, Robert D.(1988) 'SYNTHESES AND CHARACTERIZATION OF 1,3-DITHIEPIN-2-CARBODITHIOLATE AND ITS ALKYLATED DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 39: 3, 221 — 233
To link to this Article: DOI: 10.1080/03086648808072879
URL: http://dx.doi.org/10.1080/03086648808072879

Phosphorus and Sulfur, 1988, Vol. 39, pp. 221–233
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SYNTHESES AND CHARACTERIZATION OF 1,3-DITHIEPIN-2-CARBODITHIOLATE AND ITS ALKYLATED DERIVATIVES

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(Received 5 February 1988; in final form 5 February 1988)

The synthesis and characterization of a new series of organo-sulfur compounds which contain the tetrathioethylene unit are reported. A single crystal structure study of one of these compounds, 2-(1,3-dithiolan-2-ylid-ene)-1,3-dithiepin was carried out. The crystals belong to space group $P\bar{1}$ with $a = 8.634(2)$ Å, $b = 15.658(4)$ Å, $c = 8.196(2)$ Å, $\alpha = 75.79(2)°$, $\beta = 103.11(2)°$, $\delta = 102.70(2)°$, $R = 0.058$ for 1886 reflections $I > 3\sigma(I)$, and $D_x = 1.493$, $D_m = 1.46$, for $Z = 4$. The packing of molecules does show stacking with three close contacts between sulfurs having the following distances: 3.6477 Å, 3.5860 Å, and 3.5782 Å. Further characterization by ^1H and ^{13}C NMR, electrochemistry, and MO calculations show these compounds to be quite different from the parent TTF in many aspects.

INTRODUCTION

Work in these laboratories has centered on the design and syntheses of novel sulfur-containing molecules which promise to generate unique coordination chemistry with transition metals.[1–4] Early work concentrated on new dithiolate and dithiocarbamate ligands. More recently, the tremendous advancements in the area of synthetic metals, for example, (1) TTF–TCNQ as the first organic metal,[5] (2) $(TMTSeF)_2PF_6$ as the first organic superconducting sulfur based system,[7] has led us to investigate the incorporation of the "tetrathioethylene unit" into ligand systems.

The cyclopentadienedithiolate dianion ligand prepared in these laboratories earlier proved to be an important example to follow, stressing the importance of resonance stabilization in the ligand system since the first example of a 1,1-dithiolate containing the "tetrathioethylene unit", 1,3-dithiane-2-carbodithiolate,[8] did not yield stable transition metal complexes.[9] This can be explained by the fact that the 1,3-dithiane ring has no resonance stabilization as in the cyclopentadiene case. These findings eventually led to this study of the 1,3-dithiepin ring system.

The chemistry of the 1,3-dithiepin ring system is not extensively known, yet theoretical calculations have shown the mono anion to be a potential 10π-electron Huckel heteroaromatic system.[10,11] Experimental verification of this

* Author to whom correspondence should be addressed. This paper represents number 31 in the series, coordination of New Sulfur Containing Ligands.

claim has indeed shown that the 1,3-dithiepin anion shows "some" aromatic character though it seems to be small.[12,13]

The 1,3-dithiepin ring, being a potential electron acceptor, should be able to exert electronic effects on fulvalence type molecules. This has, in fact, been shown to be true. The 1,3-dithiepin ring, when incorporated into fulvalence type molecules, is able to stabilize dipolar forms by assisting delocalization of the negative charge.[14] Thus, resonance structures are proposed which incorporate into a 1,1-dithiolate, showing the similarity to the cyclopenta-diene dithiolate described earlier.

This paper reports the syntheses of 1,3-dithiepin-2-carbodithiolate and its alkylated derivatives. Characterization of these systems is based on ^{1}H NMR, ^{13}C NMR, cyclic voltammograms and the single crystal X-ray analysis of one of the derivatives, 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin.

RESULTS AND DISCUSSION

Syntheses

Dilithio-1,3-dithiepin-2-carbodithiolate is prepared from 2,2-dilithio-1,3-dithiepin and CS_2 followed by an appropriate alkyl halide as outlined in Figure 1. This synthesis is a modification of the earlier work on 1,3-dithiane.[15] A similar dianion was used successfully by Pichat and Noel in alkylation studies using 7,8-dimethyl-1,5-dihydro-2,4-benzodithiepin.[15] The necessity for this modification is based on the much more acidic nature of the C-2 proton of the 1,3-dithiepin compared to 1,3-dithiane. Attempts to synthesize the ligand in a stepwise manner resulted in an unfavourable disproportionation reaction (Figure 2) of the monoanion to yield 2 and the extremely unstable dithioacid which quickly decomposed as was shown in earlier work.[8]

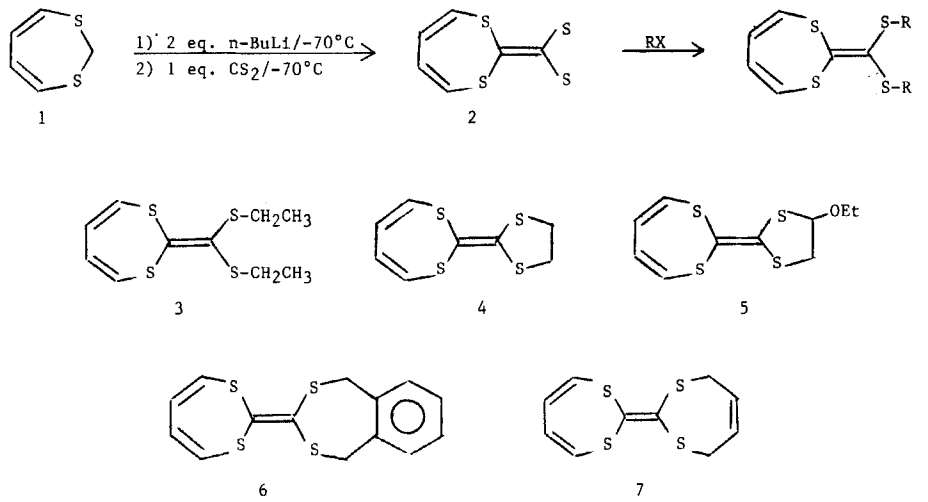

FIGURE 1 Synthesis of 1,3-dithiepin-2-carbodithiolate dianion and its alkylated derivatives.

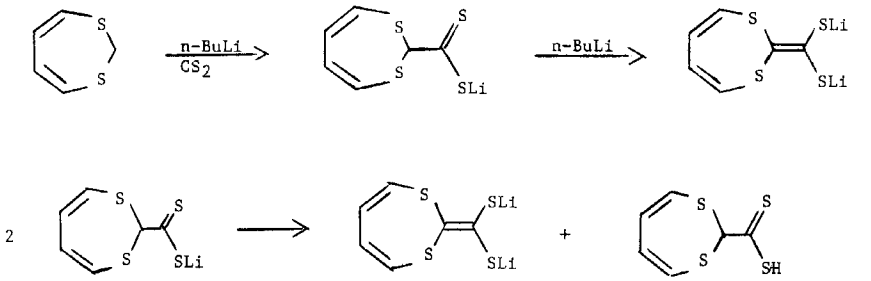

FIGURE 2 The unfavorable disproportionation reaction resulting from the stepwise synthesis of 1,3-dithiepin-2-carbodithiolate.

As a check on the dianion mechanism, the initial dianion was quenched with D_2O yielding 65–75% isolated yield of 2,2-dideutero-1,3-dithiepin (Figure 3).

Alkylation of compound 2 can be achieved easily using primary or secondary alkyl bromides or chlorides. We have found that dihalides which yield cyclic compounds are of the greatest interest due to the formation of the fulvalene type compounds with the potential of having dipolar resonance forms.

The following compounds have been prepared: 2-bis-(ethylthio)methylene-1,3-dithiepin,3; 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin,4; 2-(4-ethoxy-1,3-dithiolan-2-ylidene)-1,3-dithiepin,5; 2-(1,5-dihydro-2,4-benzodithiepin-3-ylidene)-1,3-dithiepin,6; and 2-(4,7-dihydro-1,3-dithi-epin-2-ylidene)1,3-dithiepin,7.

Attempts to synthesize the interesting dipolar compound 2-(1,3-dithiole-2-ylidene)-1,3-dithiepin using compounds **4** and **5** as precursors proved unsuccessful. Following analogous reactions from the literature, neither the oxidation of **4** with DDQ[18] nor the acid catalyzed loss of EtOH from **5**[19] led to the desired product. Instead an insoluble black polymer was isolated in both cases (Figure 4). This may, in fact, be caused by the instability or the high reactivity of the dipolar form, leading to its subsequent polymerization.

An alternative route to this class of compounds has been briefly investigated based on the Peterson olefination reaction,[20–23] shown in Figure 5. This strategy was most appealing since there are numerous substituted 2-oxo-1,3-dithioles available.[24] However, to date no success has been achieved in this area.

More recently, modification of the Peterson olefination involved coupling the anion with the triflate salt of the carbonyl compound.[25] Unfortunately, we were unable to prepare any of the triflate salts of the 2-oxo-1,3-dithiole compounds.

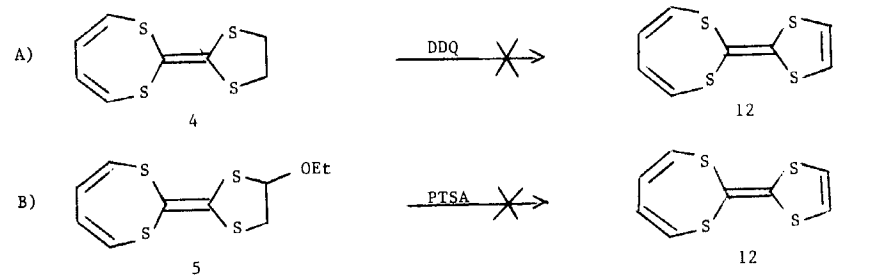

FIGURE 3 Synthesis of 2,2-dideutero-1,3-dithiepin.

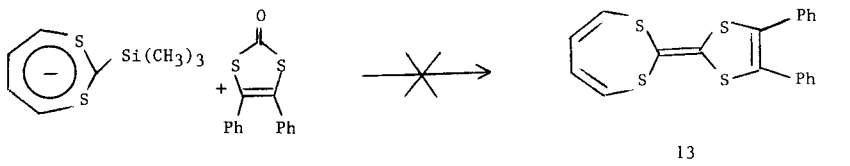

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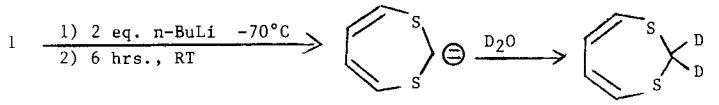
FIGURE 4 (A) Oxidation of compound **4** with DDQ, (B) treatment of compound **5** with p-TSA.



10 11

FIGURE 5 Peterson olefination type coupling reaction.

A second molecule of great interest is tetrathioheptafulvalene. This molecule can be looked upon as a potential new acceptor molecule with structural features similar to TTF. However, the extremely poor isolated yields of **7** and the inability to obtain pure products resulted in the abandonment of the stepwise synthetic approach. A second synthetic sequence is based on the photochemical 2 + 2 addition of an acetylene to TTF followed by a thermal 2 + 2 ring opening also proved to unsuccessful. This was somewhat surprising since all the π-orbital character in the LUMO of TTF is on the outer C—C double bonds and the required energy was similar to other acetylene coupling reactions.

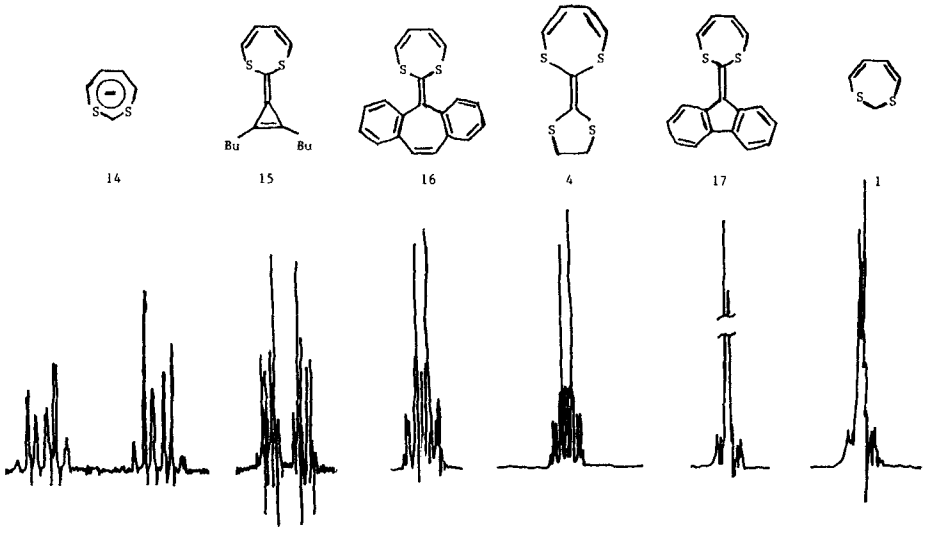
^1H and ^{13}C NMR

^{1}H NMR has become a very useful means by which one can measure the amount of electron delocalization in the 1,3-dithiepin ring. This is due to characteristic signals of the four vinylic protons in the 1,3-dithiepin moiety. The 2-H-1,3-dithiepin (Structure 1, Table I) shows the very narrow AA'BB' signals centered at $\delta = 6.31$ for the vinylic protons, whereas the same protons in the anion (Structure 14, Table I) H-5,6 centered at 5.80 ppm and the signals for H-4,7 centered at 6.63 ppm, resulting in a $\Delta\delta = 0.83$ ppm.[26] The substantial upfield shift of H-5,6 in the anion as opposed to the neutral species has been attributed to the greater charge density at these positions in the anion. Added structural information in the anion is obtained from the fine splitting of the H-4 and **7** signals of 0.8 Hz per line from the remaining proton at C-2, via long range *W*-coupling. This *W*-coupling indicates a quite planar structure. Both of these findings have helped to substantiate the claim of the anion as being a 10 π-heteroaromatic delocalized system.

Murata *et al.*[27] have incorporated the 1,3-dithiepin ring into several fulvalene type compounds with the potential for the formation of dipolar species. It was then postulated that the differences in chemical shifts between H-4 and **7**, and H-5 and **6** might serve as a measure of the anionic character of the 1,3-dithiepin moiety. Table I summarizes their results along with the incorporation of compound **4** of this work. It is clear that the degree of the chemical shift

TABLE I

Comparison of the Low Field ^{1}H NMR Splitting Patterns of Several 1,3-Dithiepin Containing Compounds (in ppm).



$\delta_{5,6}$	5.80[a]		5.96[b]		6.14[b]		6.25[c]		6.52[b]		6.29[a]
$\delta_{4,7}$	6.63		6.32		6.27		6.32		6.57		6.33
$\Delta\delta$	0.83	>	0.36	>	0.13	>	0.07	>	0.05	~	0.04

a) Semmelhack, C. L.; Chiu, I-Ching and Grohmann, K. G. *Tetrahedron Letters., 1976*, 1251–4.
b) Sugihara, Y., Fujiyama, Y., and Murata, I. *Chem. Lett.* 1980, 1427–1430.
c) This work.

difference ($\Delta\delta$) between H-4,7 and H-5,6 increases as the ability of the carbocyclic ring's electron donating ability increases. Interestingly enough is the fact that although compound **4** is not in total conjugation, it does lead to significant splitting in the vinylic region. This can be explained primarily by sulfur's ability to stabilize 'α' carbocations. Therefore, since the exocyclic double bond has two sulfurs to stabilize the dipolar form, it is not surprising that the C–C double bonds would be heavily polarized towards the dithiepin ring.

In addition to compounds **4**'s electronic accepting ability, the analysis of the AA'XX' pattern provided an accurate determination of the *J* coupling constants. It was felt that a comparison of these *J* values to those obtained for the 1,3-dithiepinyl anion would add additional information to the ring system's "aromatic" character.

Values for the four coupling constants (J_{4-5}, J_{5-6}, J_{4-6}, J_{4-7}, 10.767, 7.431, 0.039, 0.620) were obtained by use of the PANIC[28] (Parameter Adjustment in NMR Iterative Calculation) computer program, aminicomputer version of LAOCOON[29] type program provided by Dr. Charles Moreland in cooperation with Research Triangle Institute. Initial estimates of *J* values used to generate a synthetic spectrum were based on that the 1,3-dithiepinyl anion reported earlier.[30] This calculated spectrum matched to an experimental one and the program was recycled through an iterative process to provide best fit *J* coupling constants according to a least-squares criterion.

A comparison of the NMR parameters of 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin (**4**) and the 1,3-dithiepinyl anion[14] reveals values that are quite close except for $J_{5\text{-}6}$. This is the coupling dealing with the H-5,6 interaction. The coupling is much stronger in the 1,3-dithiepinyl anion and this can be easily explained by the fact that in the anion the electron density is increased at these positions due to electron delocalization. This results in a shorter C-5,6 bond allowing for a stronger coupling of their protons.

^{13}C NMR was also used as a means to determine the amount of polarization of the C—C double bond of the "tetrathioethylene unit" in these molecules. This was done by analogy to the styrene systems where the carbon with a partial positive charge will lie at higher fields. A comparison of the ^{13}C NMR resonances for compounds 3 and 4 along with several styrene examples[32] indicates that there is a tendency for the C2 carbon of the 1,3-dithiepin ring to lie at substantially lower fields in every case. However, a trend from acyclic to small ring to large ring systems does not seem to be present.

X-ray Analysis

Until now all inferences to structural planarity have been based solely on NMR data. Therefore, it was important to obtain a crystal structure of compound **4** since it gave the largest splitting in this class of compounds, in the NMR.

A view of the asymmetric unit with labelling of the atoms is shown in Figure 6.

The most interesting information from the structure determination was the non-planarity of the molecule. Plane calculations on molecules *A* and *B* in the asymmetric unit show the molecule to consist of two planes that bisect at an angle of 109.75°. Molecule *B* is similar with the 7-membered ring being less planar.

The packing diagram shows several interesting features. Although the molecules are not in segregated stacks as in TTF, they do seem to be organized in a three dimensional network. There are areas in which the "tetrathioethylene unit" seems to be stacking or actually forming a sheet-like network. At the same time, but in a crossing direction, the π-systems of the diethiepin rings seem to be aligned in a similar manner. Finally, and most importantly, there are three close contacts (per unit cell) between sulfur atoms which link these sheets together. These S—S contacts were all under the Van der Waals contact value of 3.70 Å.

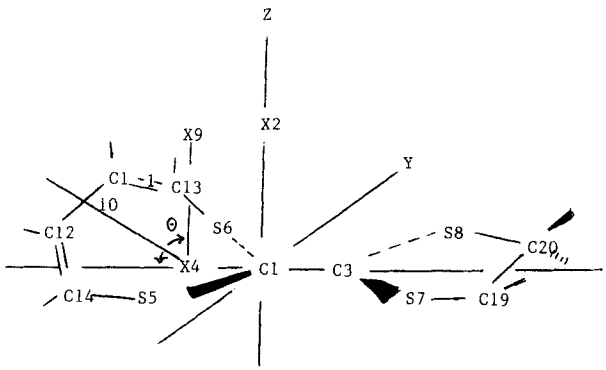


FIGURE 6 ORTEP diagram of the asymmetric unit of 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin(4).

This is similar to the three dimensional network seen in the structure of $(TMSeF)_2X$[33] salts and the two dimensional network seen in the structure of $(BEDT\text{-}TTF)_2ReO_4$.[34]

At this time a brief investigation utilizing extended Huckel methods was initiated since accurate bond angles and distances were available. It was decided to look at molecule *A* (Figure 6) since it was the most planar and to calculate the effect of flattening the ring. This was done on several values of the angle and was also carried out on the theoretical case of having the totally unsaturated compound (i.e. compound 12). Figure 7 shows the labeling of the systems and the location of the angle θ which was varied.

In both cases, flattening lowered the total energy of the system making it more stable. This is reasonable due to the overlap of the π systems, however, this also requires the C—S—C bond angle in the dithiepin ring to increase from a normal value of 102° to 122° making it highly unfavorable. More in the line with experimental results is the fact that the largest energy separation between HOMO and LUMO came at a θ value of 15°, close to experimental value of 19.75°. This work also adds additional support to the concept that the tetrathioethylene bond is heavily polarized towards the dithiepin ring since for the HOMO the largest orbital coefficient was on C-2 of the dithiepin ring.

Electrochemistry

The electrochemistry of these compounds was investigated to determine their ability to act as electron donors or acceptors. This was accomplished using cyclic voltammetry in acetonitrile solutions containing tetrabutylammonium perchlorate as the supporting electrolyte. TTF type compounds have long been studied in this manner and all exhibit similar electrochemical behavior resulting from the oxidation of the "tetrathioethylene unit" in two successive, one-electron reversible steps. Coffin[35] has tabulated reduction potentials for a series of tetrathioethylenes and Table II is a brief representation along with the experimental results obtained on these new tetrathioethylenes.

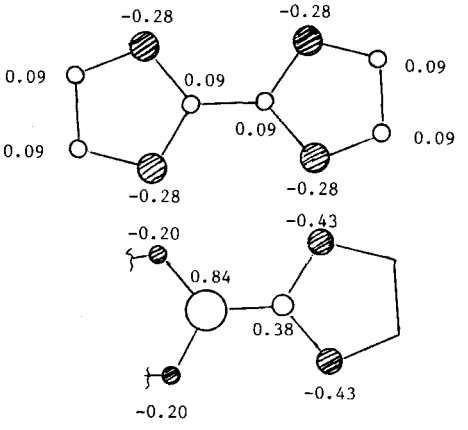


FIGURE 7 Schematic drawing of 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin showing the angle θ which is varied in the extended Huckel calculations.

In contrast to the TTF systems, those studied here are all irreversibly oxidized and lie at a much higher potential. Most striking is the fact that the tetrahydrotetra-thiofulvalene system loses both electrons around the potential where these compounds lose their one. This was indeed hard to understand since both our systems and H_4TTF can be considered as simple alkyl substituted tetrathio-ethylenes. Two possible explanations for this behavior exist.

In all the TTF type systems the molecules are basically planar and the loss of an electron results in the formation of a six π-electron system (Huckel aromatic) or one in which the lone pairs on the sulfur are aligned in such a way to help stabilize the charge by delocalization. However, in this system the tetrathioethylene unit is heavily polarized toward the dithiepin ring resulting in these electrons being held much more tightly, hence the more positive oxidation potential. This results in the formation of a reactive radical cation which undergoes chemical reaction prior to electrochemical reduction.

The molecular orbital explanation is somewhat similar. Drawings of the structures (compound 4 and TTF) along with the orbital representation for the HOMO's are given in Figure 8.

In the case of TTF, the tetrathioethylene unit is totally conjugated, whereas in the compound **4**, since the structure is bent, the sulfur of the dithiepin ring lies in the perpendicular plane in the remaining π-system resulting in loss of conjugation. This is also seen in the orbital representation of the HOMO's of the two compounds. The loss of conjugation is due to the small orbital character at the carbon positions in the dithiepin ring. The heavy polarization of the C—C double bond is shown to be as would be predicted by resonance. Loss of an electron results in the formation fo a radical cation in a system whose natural tendency would be to form a radical anion.

Examination of the trend shown in Table 2 reveals that addition of electron-donating methyl groups to TTF decreases the oxidation potential, just as loss of one double bond increases it. In this light, one would have predicted that compound **4** should have been oxidized around the same potential as H_4TTF if planar, but loss of conjugation in the bent structure increases the potential even further. This seems logical since all four new tetrathioethylene compounds have similar potentials. Compounds **4**, **5** and **6**, are basically the same with the non-dithiepin sulfur locked in position; whereas, the diethyl derivative has an even more positive potential due to the fact that the noncyclic alkylsulfides are susceptible to free rotation about a C—S bond further lowering conjugation.

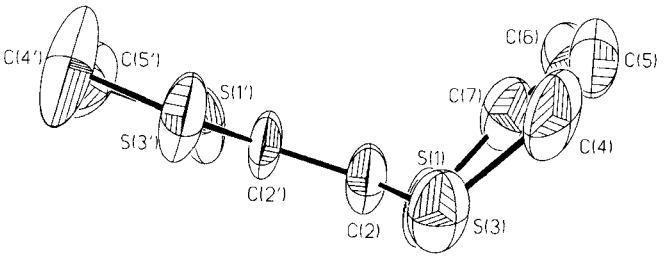
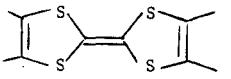
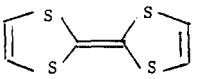
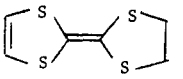
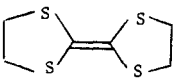
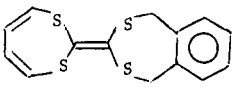
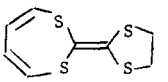
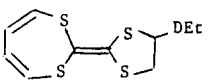
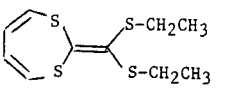


FIGURE 8 Molecular orbital representation for the HOMO of TTF (top) and 2-(1,3-dithiolan-2-ylidene)-1,3-dithiepin (bottom).

TABLE II

Oxidation potentials of several TTF derivatives along with the new tetrathioethylenes based on 1,3-dithiepin.

	E_1	E_2
	0.28	0.63
	0.33	0.70
	0.405	0.89
	0.68	1.12
	1.036	
	1.046	
	1.055	
	1.130	

CONCLUSIONS

The new potential ligand system 1,3-dithiepin-2-carbodithiolate has been prepared and characterized with organic derivatives. The structure of these derivatives has shown to be puckered by X-ray analysis. However, there does seem to be interesting aspects to the packing diagram. The presence of S—S close contacts and the presence of a systematic packing continues to make this class of compounds interesting. The electrochemical results seem to rule out the use of these compounds as potential new donor molecules; however, the NMR analysis does seem to indicate the potential for interesting electronic effects to be present due to resonance.

EXPERIMENTAL

Reagents

1,3-Dithiepin was prepared by the standard procedure in the literature[36] and stored at 0°C under argon. Argon was purchased from Air Products Inc. All chemicals were obtained from Aldrich Chemical Company unless otherwise stated. *n*-BuLi was obtained as a 2.7 *M* solution in hexane and was titrated[37] prior to use to determine the exact concentration. Tetrahydrofurna (THF) was freshly distilled under argon from Na-benzophenone just prior to use. Acetonitrile was distilled under argon from P_2O_5 just prior to use.

Physical measurements

All electrochemical measurements were performed using a BAS CV27. The electrochemical cell used for cyclic voltammetry employed a platinum electrode, and a Ag/AgCl reference electrode. Measurements were made on 10^{-3} *M* solutions in acetonitrile with 0.1 *M* tetrabutyl-ammonium perchlorate as the supporting electrolyte. Argon was passed through the solution for fifteen minutes prior to taking the measurements. IR spectra were recorded in a Perkin Elmer 521 spectrophotometer over the range 4000–300 cm^{-1} as KBr pellets or nujol mulls. NMR spectra were obtained in $CDCl_3$, employing a Bruker WM 250 for 250 MHz ^1H NMR and a JOEL PS-100 for ^{13}C NMR. Elemental analysis were obtained from Atlantic Microlabs, Atlanta, Georgia.

Syntheses

All reactions were carried out employing standard Schlenk techniques under anhydrous argon.

2,2-*Dideutero*-1,3-*dithiepin* **11**. To one gram (7.7 mmol) of 1,3-dithiepin in dry THF was added 2.25 eq. of *n*-BuLi (2.7 M in hexane) at −70°C. The solution was allowed to come to room temperature and then stirred for an additional six hours. The temperature was lowered to −70°C and the dianion was quenched with D_2O. Isolation of the product followed by chromatography over neutral alumina gave a 90% yield of a yellow oil which showed the loss of the protons at C-2. ^1H NMR ($CDCl_3$) $\delta = 6.315$.

Dilithio-1,3-*dithiepin*-2-*carbodithiolate* **2**. *n*-BuLi (13.0 ml, 2.7 M in hexane) was added to a solution of 1.5 g of 1,3-dithiepin (11.5 mmol) in 250 ml of THF at −70°C over a 10 min. period. This solution was allowed to warm to room temperature slowly over a period of one hour, then stirred for an additional six hours. At this time the deep red solution was cooled to −70°C and one equivalent of CS_2 (0.7 ml) was added. The solution was allowed to stir for an hour at −70°C then quenched with the appropriate alkyl halide.

2-*Bis*(*ethylthio*)*methylene*-1,3-*dithiepin* (**3**). 2 was prepared as above and two equivalents of ethyl bromide was added at −70°C. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was filtered free of LiBr and absorbed onto 5 g of neutral alumina. Purification by column chromatography (neutral alumina, 80/20 hexane/chloroform) followed by distillation afforded pure 3 as an orange oil: yield 60–70%; b.p. was not obtained due to decomposition above 100°C at 0.05 mm. ^1H NMR ($CDCl_3$) = 6.36 (4 H, m), 2.77 (4 H, q), 1.17 (6 H, t); ^{13}C NMR ($CDCl_3$) = 142.48 (C-2), 136.99 (C-2′); 130.94 (C-4,7), 127.50 (C-5,6); 29.24 (CH_2), 14.50 (CH_3). IR (cm^{-1}) = 2960, 2920, 2860, 1565, 1445, 1410, 1370, 1330, 1225, 1050, 960, 845, 750, 710, 660, 530, 500.

2-(1,3-*Dithiolan*-2-*ylidene*)-1,3-*dithiepin* (**4**). **2** was prepared as above and one equivalent of anhydrous ethylene bromide was added at −70°C. Following the same reaction conditions, workup, and purification by column chromatography followed by recrystallization from absolute ethanol afforded pure 4 as light yellow crystals: yield 55–65%; m.p. 88–89°C. ^1H NMR ($CDCl_3$) $\delta = 3.51$ (4 H, s) 6.27 (4 H, m,-AA′BB;); ^{13}C NMR ($CDCl_3$) $\delta = 40.13$, 108.035 (C-2′), 126.59 (C-5 and 6), 127.32 (C-4 and 7), 155.61 (C2). Anal. Calcd. for $C_8H_8S_4$: C, 41.35; H, 3.47; S, 55.18. Found: C, 41.37; H, 3.47; S, 55.12. IR (cm^{-1}) = 3040, 2940, 1570, 1500, 1420, 1390, 1345, 1285, 1250, 1150, 1110, 980, 945, 860, 845, 740, 690, 675, 480.

2-(4-*Ethoxy*-1,3-*dithiolan*-2-*ylidene*)-1,3-*dithiepin* (**5**). 2 was prepared as above and one equivalent of anhydrous 1,3-dichloroethyl ethyl ether was added at −70°C. Following the same reaction conditions, workup, and purification as above afforded 5 as light yellow plates: yield 55–60%, m.p. = 109.5–110.5°C. ^{1}H NMR ($CDCl_3$) δ = 1.25 (3 H, t), 3.48 (2 H, m, S-CH_2), 3.79 (2 H, m, O-CH_2), 5.55 (1 H, m) 6.27 (4 H, m,-ABCD). ^{13}C NMR ($CDCl_3$), δ = 14.68 (-CH_3), 46.12 (S-CH_2), 65.15 (O-CH_2), 92.94 (CH), 126.83 and 126.63 (C-5 and 6), 127.27 and 127.17 (C-4 and 7). Anal. Calcd. for $C_{10}H_{12}S_4O$ C, 43.45; H, 4.37; S, 46.39. Found: C, 43.39; H, 4.37; S, 46.46. IR (cm^{-1}) = 2990, 2940, 2880, 1570, 1500, 1420, 1380, 1315, 1180, 1120, 1080, 1030, 995, 980, 870, 840, 740, 700, 660, 525, 480.

2-(1,5-*Dihydro*-2,4-*benzodithiepin*-3-*ylidene*)-1,3-*dithiepin* (**6**). 2 was prepared as above and one equivalent of α,α'-dibromo-*o*-xylene was added as a solution in 50 ml of THF at −70°C. Following the same reaction conditions, workup, and purification (recrystallization from chloroform/ethanol) afforded pure 6 as a light yellow solid: yield 45–55%, m.p. = 119.5–120.5°C. ^{1}H NMR ($CDCl_3$) δ = 4.26 (4 H, s), 6.37 (4 H, m), 7.17 (2 H, m), 7.19 (2 H, m); ^{13}C NMR δ = 37.95, 127.59, 129.49, 129.76, 135.64, 143.47. Anal. Calcd. for $C_{14}H_{12}S_4$: C, 54.51; H, 3.92; S, 41.57. Found: C, 54.51; H, 3.97; S, 41.48. IR (cm^{-1}) = 3020, 2950, 1560, 1490, 1480, 1445, 1400, 1380, 1335, 1300, 1250, 1200, 940, 865, 845, 830, 755, 715, 660, 575, 530, 490, 420.

2-(4,7-*Dihydro*-1,3-*dithiepin*-2-*ylidene*)-1,3-*dithiepin* (**7**). 2 was prepared as above to which was added one equivalent of cis-1,4-dichloro-2-butene. Following the same reaction conditions, workup, and purification yielded a light yellow oil, which contained minor impurities which could not be removed by repetitive chromatography. Yield was 5% and a b.p. was not obtained due to decomposition. ^{1}H NMR ($CDCl_3$) δ = 3.55 (4 H, d), 5.66 (2 H, t), 6.32 (4 H, m); ^{13}C NMR in ($CDCl_3$) δ = 31.36 (C-4′, 7′), 118.27 (C-2′), 127.12 (C-5, 6), 127.33 (C-4, 7), 129.29 (C-5′, 6′), 133.43 (C-2). IR (cm^{-1}) = 2960, 2920, 2860, 1560, 1445, 1410, 1360, 1330, 1250, 1080, 1050, 1020, 960, 930, 845, 830, 750, 710, 655, 530, 500.

Reaction of 2-(1,3-*dithiolan*-2-*ylidene*)1,3-*dithiepin with* 2,3-*dichloro*-5,6-*dicyano*-1,4-*benzoquinone* (*DDQ*). To 1.0 g (4.3 mmol) of compound 4 in 250 ml of hot xylene was added 3.5 equivalent of DDQ in 100 ml of the same solvent while under argon atmosphere. After 25% of the DDQ had been added, the solution turned black and a dark solid precipitated from the solution. Workup of the reaction afforded an insoluble black polymeric material. Varying amounts of DDQ led to the same results, therefore, the reaction was abandoned.

Reaction of 2-(4-*ethoxy*-1,3-*dithiolan*-2-*ylidene*)-1,3-*dithiepin with p-toluenesulfonic acid.* One gram (3.6 mmol) of compound 5 and one equivalent of PTSA were added together in dry toluene and heated to reflux under an argon atmosphere. As the reaction mixture reached reflux, the solution turned black with the formation of a solid crust around the sides of the flask. Isolation of the yellow solid yielded an insoluble black polymer. Varying amounts of acid used or using benzene instead of toluene had no effect on the outcome of the reaction.

Attempted synthesis of 2-(4,5-*diphenyl*-1,3-*dithiole*-2-*ylidene*)-1,3-*dithiepin* (**12**) *via Peterson olefination.* To a stirred solution of 1,3-dithiepin in 100 ml of dry THF was added, under argon at −70°C, one eq. of 2.7 *M* *n*-BuLi in hexane. The reaction mixture was allowed to stir at room temperature for one hour. An equivalent of trimethylsilyl chloride was added to the solution at −70°C and the reaction mixture was stirred at room temperature for one hour. The resulting solution was again cooled to −70°C and a second eq. of *n*-BuLi was added. The reaction mixture was allowed to warm to room temperature and stir for an additional hour. The reaction mixture was cooled to −70°C and one equivalent of 4,5-diphenyl-1,3-dithiol-2-one was added in one portion. The solution was allowed to warm to room temperature and stir for an additional hour. The reaction mixture was then poured into ice water. The organic material was extracted repeatedly with ether. The ether layers were combined, dried over anhyd. $MgSO_4$ and evaporated off. The oily residue was chromatographed (neutral, alumina, 10% chloroform in hexane) to give a deep red-black oil. TLC showed many spots. ^{1}H NMR gave no indication of coupling.

Attempted synthesis of 4,5-*diphenyl*-2-*methoxy*-1,3-*dithiole.* To a solution of 4,5-diphenyl-2-methoxy-1,3-di-thiole in 10 ml of dry ethylene chloride was added 1.1 eq. of methyl triflate while stirring at room temperature. After completion of the addition, the mixture was heated to reflux for one hour, then allowed to cool slowly. No crystals appeared, removal of solvent yielding starting materials. Long reaction times and excess triflate did not help. Reaction was abandoned.

Single-Crystal X-ray Analysis

Light yellow, prismatic crystals of 4 suitable for X-ray analysis were grown by the slow evaporation of an absolute ethanol solution. Professor Jon Bordner carried out the structure study. A representative crystal ($0.22 \times 0.23 \times 0.29$ mm) was mounted and encased in fast-setting epoxy resin. The crystal was surveyed and a 1-Å data set (maximum $\sin\theta/\lambda = 0.5$ was collected on a Syntex P1 diffractometer. The diffractometer was equipped with a graphite monochromator and copper radiation ($\lambda = 1.5418$ Å). All diffractometer data were collected at room temperature. Atomic scattering factors for carbon and sulfur were taken from the *International Tables for X-ray Crystallography,*[38] except hydrogen which was taken from Stewart, Davidson and Simpson.[39] All crystallographic calculations were facilitated by the CRYM computer library.[40] Absorption corrections were not applied due to the unknown absorption of the epoxy resin.

A trial structure was obtained by direct methods using the MULTAN program.[41] It was necessary to first determine the trial structure in the space group P1 and then convert it to the space group $P\bar{1}$. This trial structure refined routinely. Hydrogen positions were calculated. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of full-matrix least-squares refinement contained the scale factor, secondary extinction coefficient, coordinates, and anisotropic temperature factors in a single matrix. The shifts calculated in the final cycle were all zero. The full-matrix routine minimized, $\Sigma w(F_o^2-F_c^2)^2$ were $w = 1/\sigma^2 (F_0)^2$ based on $\sigma^2 (I) = S + \alpha^2 (B1 + B2) + (dS)^2$. The final R-index was 0.058. A final difference Fourier revealed no missing or misplaced electron density.

The refined structure was plotted using the ORTEP computer program of Johnson.[42*]

ACKNOWLEDGMENTS

Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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