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Tetrathiafulvalene Quinones, Hydroquinones and Esters

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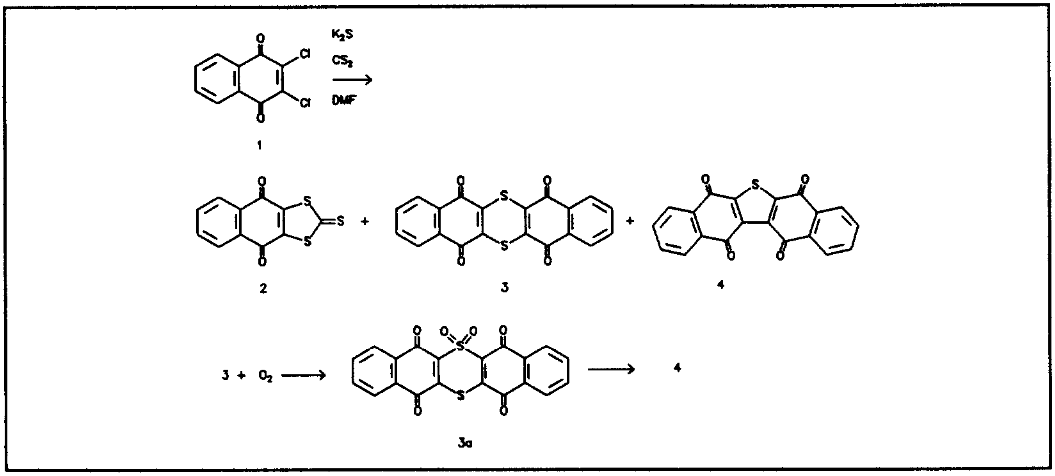
Abstract: Benzocyclohexa-2,5-diene-1,4-dione-1,3-thiole-2-thione (**2**) was synthesized starting with 2,3-dichloronapthoquinone (**1**) Compounds **3** and **4** were also obtained, however, the yield of **2** can be increased through control of the temperature and reaction time Reaction of **2** with triethylphosphite gave **5** and the tetrathiafulvalene ester **6**. The tetrathiafulvalenequinone (**9**) was obtained by hydrolysis of **6** followed by oxidation of **8**. Compound **9** was obtained more directly by hydrogenation of **2** followed by coupling with triethylphosphite and oxidation Chloranil was used to prepare the dithiafulvene quinone **12** which was reduced, coupled with triethylphosphite to form, presumably, polymer **13** The reactions were repeated using the hexanoic acid esters of the corresponding hydroquinone thiafulvalenes The crystal structures of **2**, **3**, **4**, **5**, **6a** and **10** were determined by X-ray diffraction Cyclic voltammetry studies show the tetrathiafulvalene quinones reduce like quinones, but do not exhibit the oxidation properties of tetrathiafulvalenes

INTRODUCTION

Charge-transfer (CT) complexes and radical cation salts derived from TTF, BEDT-TTF and derivatives exhibit high electrical conductivities including some which are superconductors [1] The oxidation potentials of the donors and the ability to form partially filled conduction bands, e.g. $(\text{BEDT-TTF})_2{}^{+}A^{-}$, are essential to good electrical conductivity. The good conductors crystallize in segregated stacks of donors and acceptors with numerous short donor inter- and intra-stack interactions between sulfur atoms to increase the dimensionality of the charge-carrier transport Several groups have attempted to increase the dimensionality by extending the π-conjugation through oligomerization and condensation [2] Our interest in quinones and in organosulfur chemistry led us to investigate the extension of the π-system by the incorporation of quinone moieties. Since TTF and related molecules are easily oxidized and quinones easily reduced, what physical properties might arise from a combination of these moieties? In this paper we discuss our initial attempts at synthesis and characterization of these systems.

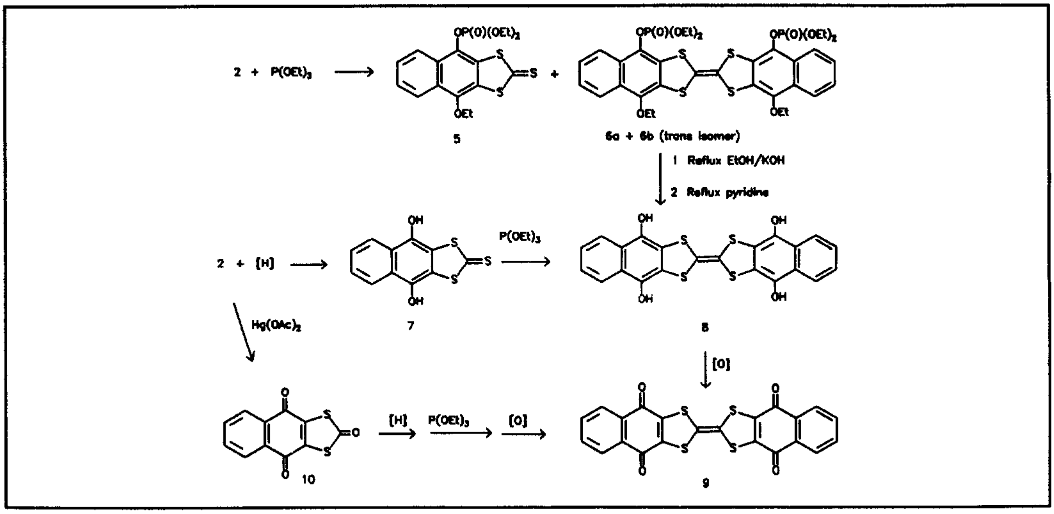
DISCUSSION:

The reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with K_2S and CS_2 in DMF leads to the formation of the desired 1,3-thiole-2-thione derivative (**2**) (Scheme 1), however, compounds **3** and **4** are also recovered Although no attempt was made to maximize yields, the formation of compound **2** is favored by lower temperatures and shorter reaction times Compound **4** probably arises from the air oxidation of **3** via the sulfone **3a**, however, it has been suggested that the bis(sulfoxide) is the intermediate in this reaction [3] In systems of this sort the formation of a sulfone or bis(sulfoxide) is dependent upon the nature of the oxidant[4]



Scheme 1

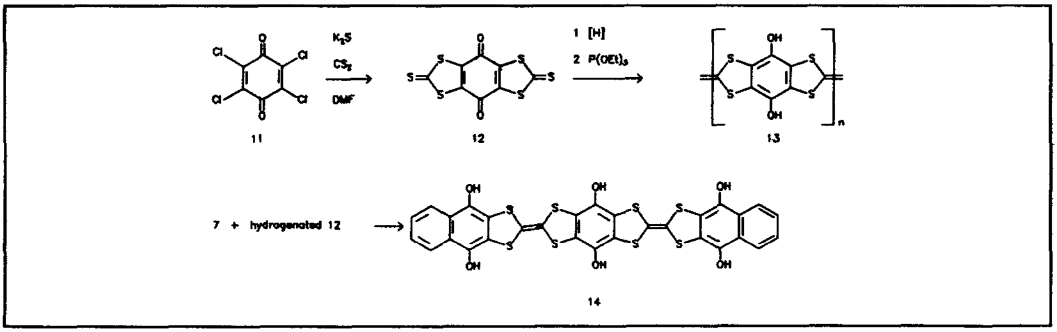
No oxidized product was isolated under the reaction conditions; however, nucleophilic oxidation of 3 leads to an intermediate with an unsymmetrical ^{13}NMR spectrum which is consistent with 3a. The crystal structures of compounds 2, 3, and 4 were determined.



Scheme 2

Reaction of 2 with excess triethylphosphite leads first to the reduced ester 5 followed by coupling to give the two isomers 6a and 6b (Scheme 2) The desired coupled product 9 can be prepared by removing the phosphate and ethyl groups to give the hydroquinone 8 followed by oxidation. An easier procedure is to reduce compound 2 to 7 which can be coupled by triethylphosphite to give 8 and oxidized to 9 Compound 9 was prepared also via 10 which was obtained from 2 upon reaction with $Hg(OAc)_2$ The crystal structures of 5, 6a, and 10 were determined Compounds 8 and 9 are only slightly soluble and no suitable single crystals could be obtained.

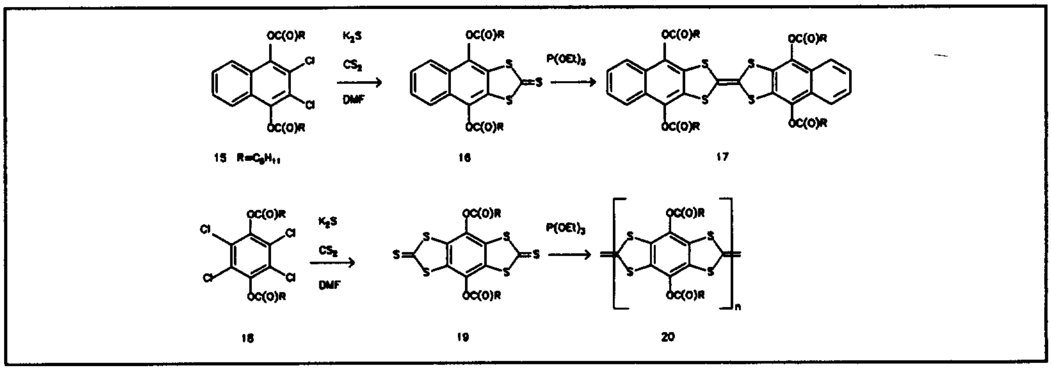
Tetrathiafulvalene (TTF), BEDT-TTF and dibenzotetrathiafulvalene (DBTTF) readily form charge-transfer salts, and exhibit two oxidation waves in DMF. Compound 2 exhibits no oxidation wave; however, there are four reduction waves with $E^\circ_{1/2}$(SHE) = -0.284, -0.628, -1.055 and -1.380 V, Table 1. Compound 10, with oxygen in place of sulfur, gives two reduction waves, $E^\circ_{1/2}$ = -0.365 and -1.246 V. Compound 9 exhibits a reduction wave at -0.320 V, however, at both negative and positive potentials the current increases sharply with increasing voltage giving no distinct oxidation-reduction couples. Attempts to prepare, by electrocrystallization techniques, single crystals of charge transfer salts using 9 as either the cation or anion were unsuccessful. A small quantity of fine black powder was recovered after some experiments.



Scheme 3

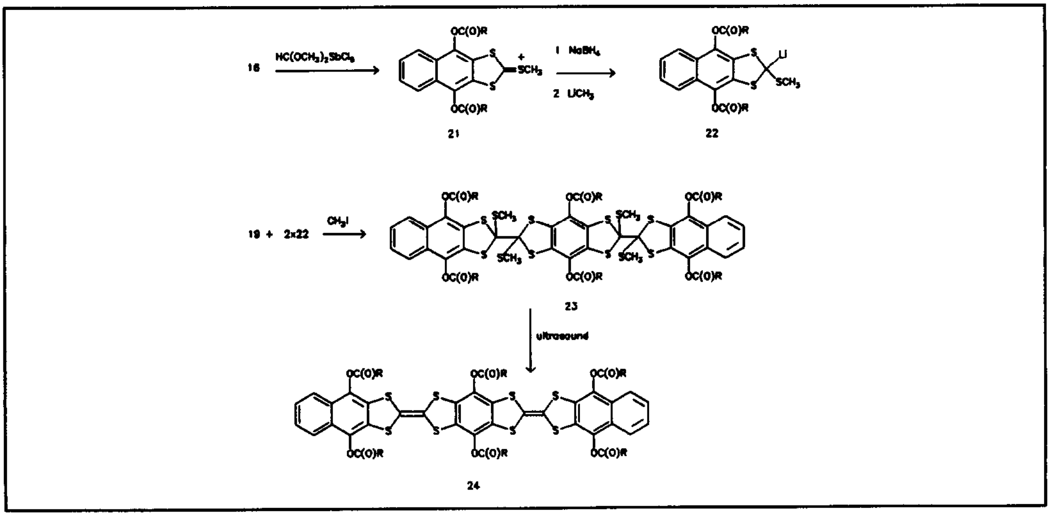
Compound 12 was prepared from chloranil, 11, and upon reduction and coupling with triethylphosphite produced a black insoluble material, presumably 13, which could not be characterized. Attempts to solubilize the product with trialkylsilylchlorides was unsuccessful. Compound 12 was reduced, reacted with trimethylsilylchloride, and coupled with triethylphosphite. The coupled but partially hydrolyzed material was completely hydrolyzed yielding a black insoluble powder. Pressed pellets gave an electrical conductivity of about 0.01 S cm^{-1} which increased by a factor of at least 10^2 upon exposure to iodine vapor. Although it is assumed the product is polymeric, no estimate of chain length or molecular weight distribution could be made. Compound 7 and hydrogenated 12 were coupled with triethylphosphite in an attempt to prepare 14. Although a small quantity of 8 was recovered the majority of the material was too insoluble for characterization.

To improve the solubility and permit easier separation of products, the starting quinones were reduced and reacted with hexanoyl chloride, see Scheme 4. Compound 16 was coupled with triethylphosphite to give a bright yellow compound 17 with no hydrolysis or no additional reaction products with triethylphosphite. Compound 17 can be hydrolyzed to give 8. Compound 19 is coupled by triethylphosphite to give a slightly soluble dark reddish-brown compound presumably with structure 20; however, no estimate of molecular weight distribution was made. No C=S ^{13}C resonances are observed, however, due to low solubility and the inherent weakness of the signal from this carbon atom, the chain length would not have to be large. Esters 17 and 19 exhibit two oxidation waves, however no single crystals were obtained during electrocrystallization studies.



Scheme 4

Compound 16 was converted into the dithiolium salt 21 via treatment with dimethoxycarbonium pentafluorantimonate.[5] Treatment with NaBH$_4$ and methyllithium in THF[6] yielded compound 22, probably with some hydrolysis of the ester Reaction of a 2 1 mixture of 22 and 19 with CH$_3$I yielded a reddish brown solid which was a mixture of 23 and partially hydrolyzed product Removal of the methylsulfide



Scheme 5

groups by ultrasonic sound[6b] at 70°C was incomplete; however, complete conversion was achieved by refluxing in 1,1,2,2-tetrachlorethane with a trace of p-toluenesulfonic acid The complex mixture was reacted with hexanoyl chloride to simplify the product distribution, and a reddish-brown material was isolated whose spectrum is consistent with structure 24

Table I. Half-wave Potentials $E°_{1/2}$(NHE)[a,b] for compounds 2, 7, 9[c], 10, 17[d], and 19.

	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$		$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
2	-0.284	-0.628	-1.055	-1.380	7	=0.04	-1.400		
9	-0.320				17	+1 115	+0.935	-.302	
10	-0.365	-1.245			19	+0.455	+0.090	-.418	-1.680

a. 1 0 mm diameter Pt wire working electrode; Ag wire as a quasi reference electrode; Cp_2Fe as an internal standard,[13] 0 10 M $TBAClO_4$ in DMF or acetonitrile. b Most of the oxidation-reduction waves are not reversible. c. The CV shows large current increases at the extreme oxidation-reduction potentials with poorly defined irreversible waves at about $E°_{1/2}$ of +0 50 and -0 90 V d A 9 1 toluene/acetonitrile mixture used as solvent.

EXPERIMENTAL

A mixture of 33.5 g of K_2S (42-45%, 13 mol), 15 mL of CS_2 (19 g, 0.25 mol) and 75 mL of DMF was stirred at rt for 2 h[7] To the stirred suspension of potassium trithiocarbonate was added 28.38 g (0 125 mol) of 2,3-dichloro-1,4-naphthoquinone (1) The solution was stirred at rt for 30 m resulting in a brick-red precipitate which was recovered by filtration The filtrate was extracted with CH_2Cl_2 and the evaporated residue added to the precipitate The material was chromatographed over silica gel using CH_2Cl_2 as eluent yielding 27 96 g (85% yield) of 2, 2.82 g (6% yield) of 3, and 1 88 g (4% yield) of 4 When the initial reaction mixture was stirred at 45 - 50°C for 16 h identical purification procedures yielded 6 11 g (13% yield) of 2, 29.76 g (63% yield) of 3, and 2.82 g (6% yield) of 4.

Benzocylohexa-2,5-diene-1,4-dione-1,3-thiole-2-thione (2). m p 160-162°C. MS 264(29, M+), 76(100). ^{13}C NMR($CDCl_3$). δ, 204 91, 174 94, 149.94, 134 76, 131 81, 127 53 Anal. Calcd for $C_{11}H_4O_2S_3$ C, 49 98, H, 1.53 Found C, 49 90; H, 1.55

5,7,12,14-Tetrahydrodibenzo[b,i]thianthrene-5,7,12,14-tetraone (3). m p. 316-319 °C (lit[3] 318°C), MS 376(89,M+), 76(100) Anal Calcd for $C_{20}H_8O_4S_2$ C,63 82, H,2.14 Found C,63 78, H,2 01

5,7,12,13-Tetrahydrodinaphtho[2,3-b:2',3'-d]thiophene-5,7,12,13-tetraone (4). m.p 290 °C (lit[3] 288 °C) MS 344 (100,M+) Anal. Calcd for $C_{20}H_8O_4S$ C, 69 76, H, 2.34 Found C, 69 90; H, 2.17

(1-Ethoxynaphtho[2,3-d]-1-ol)-1,3-thiole-2-thione bis(ethyl)-phosphate (5). 0 132 g (0.5 mmol) of 2, 1 mL (5 mmol) of triethylphosphite, and 20 mL of benzene were refluxed under N_2 for 3 h The solvent was removed on a rotary evaporator and the reddish residue, dissolved in methylene chloride, was chromatographed over silica gel giving 0 173 g (87%) of 5, m p 95 °C. MS 430(77,M+), 109(100) ^{13}C NMR 212.37, 144 87, 127 35, 127 15, 122 53, 121 76, 70 63, 65.53, 65 45, 16 22, 16 13, 15 91 Anal Calcd for $C_{17}H_{19}O_3S_3P$ C, 47 43, H, 4 45 Found C, 47 55, H, 4 47

Di-(syn/anti)-(1-ethoxynaphtho[2,3-b:2',3'-h]-3-ol)tetrathia-fulvalenedibis(ethyl)phosphate (6a & 6b). 0 264 g (1 mmol) of 2, 5 mL (25 mmol) of triethylphosphite and 20 mL benzene were refluxed under a N_2 atmosphere for 3 h. The orange solid was filtered, dissolved in methylene chloride and chromatographed over silica gel yielding 0 76 g (95%) **6a & 6b**, m p (**6a**) 129 °C. MS 688(1), 99(100) ^{13}C NMR($CDCl_3$)(**6a**,**6b**) δ, 145 47, 128.15, 128.08, 127 71, 127 11, 127.05, 126 91, 126.49, 126 40, 121 89, 121 19, 69 43, 69 21, 65 38, 65.30, 65 27, 64 95, 16.21, 16 12, 15 90, 15 84, 15 79, 15 64 Anal Calcd for $C_{34}H_{38}O_{10}S_4P_2$ C, 51 25, H, 4 81. Found C, 51 35, H, 4 92

Benzocyclohexa-2,5-diene-1,4-dihydroxy-1,3-thiole-2-thione (7). 2.64 g (10 mmol) of 2 was dissolved in 50 mL of 95% ethanol. A stream of N_2 was bubbled through the solution while a 4% aqueous solution of sodium dithionite was added dropwise[8] until the solution changed from pink to a light green The solution was stirred for an additional 30 m, then poured into 100 mL of water and the mixture extracted with methylene chloride The extract was dried ($MgSO_4$), and the solvent removed in vacuo at rt to give 2.58 g (97%) of light yellow-green solid 7, m p 222 - 224 °C. (A quantitative yield can be obtained also by adding an aqueous solution of $Na_2S_2O_4$ to a separatory funnel containing an ether slurry of 2. After separation, the ether layer is washed with a brine solution , dried ($MgSO_4$), and the ether evaporated) MS 266(12,M+), 76(100) ^{13}C NMR(acetone-d_6) 206 53, 139.73, 126 88, 125 72, 122.29, 122.22 Anal Calcd for $C_{11}H_6O_2S_3$ C, 49 60; H, 2 27 Found C, 49.88, H, 2.23

bis(1,4-Dihydroxynaphtho)tetrathiafulvalene (8). 2.66 g (10 mmol) of 7 was dissolved in 20 mL of benzene and 5 mL (25 mmol) of freshly distilled triethylphosphite was added slowly. The solution was refluxed under an N_2 atmosphere for 3 h The solvent was removed and the dark green solid was dissolved in methylene chloride and chromatographed over silica gel to give 2.20 g (94%) of 8, m.p. 216-218 °C. MS: 270(5), 104(100) ^{13}C NMR(acetone-d_6). 139.79, 126.94, 125.81, 124.76, 122.30. Anal. Calcd for $C_{22}H_{12}O_4S_4$: C, 56.39; H, 2.58. Found· C, 56.13; H, 2.62.

bis(1,4-Naphthoquinone)tetrathiafulvalene (9). 0.47 g (1 mmol) of 8 was suspended in 10 mL of 95% ethanol and 10 mL of 5% commercial bleach was added. The solution was stirred vigorously for 30 m. A black solid was recovered upon reduction of solvent volume to give 0.41 g (87%) of 9, phase transition 82°C m.p > 300°C Compound 9 was obtained also from compound **6a/6b**. A mixture of 0.80 g (1 mmol) of **6a/6b** in 35 mL of 95% ethanol containing excess (1.3 g) potassium hydroxide was refluxed for 20 h to remove the diethylphosphates.[9] The resulting solution was acidified with concentrated HCl and poured into water yielding a light green powder The powder was refluxed for 12 h in pyridine under N_2 to remove the ethyl ester[10] yielding compound 8. Compound 8 was converted to 9 by the procedure described above. MS: 464(3,M+), 76(100) ^{13}C NMR($CDCl_3$) 174 92, 149 95, 134 81, 131 78, 127 57 Anal Calcd for $C_{22}H_8O_4S_4$ C, 56.88, H, 1 74 Found· C, 56 94, H, 1 70.

Benzocyclohexa-2,5-diene-1,4-dione-1,3-thiole-2-one (10). To a boiling solution of 1 32 g (5 mmol) of 2 in 450 mL of dichloromethane were added 300 mL of glacial acetic acid and 2.5 g (7.8 mmol) of $Hg(OAc)_2$. The mixture was refluxed for 10 m and the solution turned from brown to pale yellow[11] The solution was filtered, and the filtrate washed with water and dried ($MgSO_4$) The solution volume was concentrated to 10 mL and a pale yellow powder developed after standing at rt. *After filtration, the powder was dissolved in dichloromethane and chromatographed over silica gel giving* 1.10 g (89%) of pale yellow 10, m p 166 - 164 °C. MS· 248(55,M+), 104(100) ^{13}C NMR($CDCl_3$)· 183 80, 175.52, 143.22, 134 60, 131 81, 127 43 Anal Calcd for $C_{11}H_4O_3S_2$. C, 53 22, H, 1 62. Found C, 53 20; H, 1 65

4,8-Dihydroxy-1,3,5,7-tetrathia-1,2,3,5,6,7-hexahydro-s-indacene-2,6-dithione (12). 0 236 g (1 mmol) of chloranil, 11, in 20 mL of DMF was added dropwise to a solution of 6.7 g K_2S (42-45%, 27 mmol) and 7.5 ml CS_2 (9.5 g, 125 mmol) in 35 mL of DMF The solution was stirred vigorously for 1 h, and a brick-red precipitated was collected and dried in a vacuum oven overnight yielding 0 28 g (88%) of 12, m p 295 - 298 °C. MS 320(100). ^{13}C NMR(DMSO-d_6) 221 46. 175 12, 162.56 Calcd for $C_8S_6O_2$ C, 29 99 Found C, 29 78.

Polymerization of 12. 100 mg of 12 was reduced with sodium dithionite to give the sparingly soluble hydroquinone A slurry of the hydroquinone in 25 mL of benzene was refluxed for 4 h with an excess of triethylphosphite yielding 65 mg of an insoluble compound 13, m.p > 300°C. Anal Calcd for $C_8H_2O_2S_4$. C, 37 19 Found C, 35 33 (A ratio of 3 units of 13 to 1 unit of 12 has C = 35 02%) 150 mg of the hydroquinone of 12 was reacted with trimethylsilylchoride[12] yielding a dark reddish-brown solution The TMS derivative was isolated (waxy solid), dissolved in 30 mL of benzene and refluxed with triethylphosphite for 3 h About 80 mg of a gummy solid was recovered, placed in dilute HCl and refluxed for 2 hrs to insure that any remaining ester was hydrolyzed. About 80 mg of a finely divided black powder, m p > 300°C was recovered. Found C, 36.3% No further purification or characterization was attempted

Attempts to prepare 14 by direct reaction. Compound 7 and the hydroquinone of 12 were mixed in a 2 1 ratio, partially dissolved in benzene and refluxed with triethylphosphite for 3 h. Although reaction occurred, only a small quantity of 8 could be recovered due to insolubility of the products. (Separation of the trialkylsilyl derivatives should be possible, however, the n-hexanoate 24 was prepared by an alternate route)

2,3-dichloro-1,4-dihydroxynaphthyl hexanoate (15) To a slurry of 9 08 g (40 mmol) of 2,3-dichloronaphthoquinone and 200 mL ethyl ether was added 8 70 g (40 mmol) of $Na_2S_2O_4$ in water, and the hydroquinone isolated by the alternate procedure described for 7 To 4 58 g (20 mmol) of the hydroquinone in 300 mL of dry CH_2Cl_2 and 2 mL of pyridine was added dropwise 6 0 g (45 mmol) of hexanoyl chloride The solution was stirred at rt for several h and was then extracted with water followed by a saturated brine solution The original water layer was extracted twice with CH_2Cl_2 and the organic layers combined. The solvent volume was reduced and compound 15 was obtained upon standing, 7 33 g (87% yield), mp 185-188 °C. ^{13}C NMR($CDCl_3$)· 179 84, 176 03, 143 45, 134 68, 130 91, 127 83, 33 99, 31 21, 24 37, 22 30, 13.89 Calcd for $C_{22}H_{26}O_4Cl_2$ C, 62.12, H, 6.16 Found C, 62 45, H, 5 96

1,4-Dihydroxynapthyl-1,2-thiole-2-thione hexanoate (16) 4 25 g of 15 were added at rt with stirring to a slurry of 2.2 g K_2S and 15 mL CS_2 in 20 mL of DMF After 2 h the solution was blood red with a greenish slurry The slurry was filtered and the red solution diluted with dichloromethane A white precipitate of starting material was removed. The compound was also obtained by the reduction of 2 followed by reaction with hexanoyl chloride.

10.2 g (38 mmol) of 1,4-dihydroxynapthalene-1,2-thiole-2-thione in dry CH_2Cl_2 with 2 mL of pyridine was stirred and 10 8 g (80 mmol) of hexanoyl chloride was added dropwise at rt. After 2 h the greenish-yellow solution was washed twice with water, then with a saturated brine solution and filtered through $MgSO_4$ The volume was reduced until a slurry began to form. Ethyl ether was added and greenish-yellow microcrystals were deposited The solution was filtered and the crystals washed with diethyl ether to yield 6.784 g (38% yield), mp 119-120 °C. MS m/z(relative intensity) 462 (6,M+), 276(100) ^{13}C NMR 210 43, 170 42, 136.21, 131 28, 127.65, 126.72, 121 18, 33 83, 31 29, 24 66, 22.28, 13 91 Calcd for $C_{23}H_{26}O_4S_3$ C,59 71, H, 5.66, S, 20 79. Found C, 59.37, H, 5 89; S, 21 0

Bis-(1,4-dihydroxynaphthol)tetrathiafulvalyl hexanoate (17). To 0.902 g (3 4 mmol) of **16** in 50 mL of benzene was added 10 mL of triethylphosphite and the solution refluxed under N_2 for 3 hrs 0 86 g (86%) of yellow product **17** was recovered, mp 200-204°C. ^{13}C NMR($CDCl_3$) 170 48, 153.86, 137 24, 128.03, 126.90, 120 80, 120 73, 33 95, 31 39, 24 75, 22.39, 13 03. Calcd for $C_{46}H_{52}O_8S_4$. C, 64.16, H, 6.08, S, 14 89 Found C, 64 23, H, 6.53, S, 14 13 Compound **17** was prepared also by reaction of **8** with hexanoyl chloride The physical and spectral properties were identical

Tetrachloro-1,4-dihydroxybenzyl hexanoate (18) 2.48 g (10 mmol) of 2,3,5,6-tetrachlorobenzhydroquinone, obtained by reduction of chloranil with sodium dithionate, was added to 70 mL of dry CH_2Cl_2 and 3.0 g (22 mmol) of hexanoyl chloride and a few drops of pyridine were added The solution was refluxed overnight. After cooling the solution was washed in a separatory funnel with water and then a saturated brine solution From the organic layer was obtained 1 38 g (31% yield) of **18**, m p 88-89 °C. ^{13}C NMR($CDCl_3$) 169 56, 143 54, 127 24, 33 59, 31 18, 24 41, 22.27, 13 89 ^{1}H NMR 2 675(t,2H), 1 814(m,2H), 1 405(m,4H), 0 934(t,3H)

4,8-Dihydroxy-1,3,5,7-tetrathia-1,2,3,5,6,7-hexahydro-s-indacyl-2,6-dithione hexanoate (19) To 4 4 g (10 mmol) of **18** was added a mixture of 2 2 g K_2S (8.5 mmol) and 15 mL CS_2 (19 g, 25 mmol) in 20 mL DMF The solution was stirred vigorously at reflux until it turned blood red (approximately 2 h) Dichlormethane was added and the solvent removed The material was eluted from a Silica gel column using CH_2Cl_2 giving a greenish-yellow solution which upon reduction in volume yielded a yellow powder, 1 0 g (19.2% yield), mp 89-92°C. The compound was also prepared by the reaction of 5 38 g of reduced **12** with hexanoyl chloride to yield 3 89 g of **19** (45% yield) ^{13}C NMR(CDCl3) 206 99, 180 54, 168.93, 134 51, 34 80, 31 20, 24 35, 22 29, 13 86. Calcd for $C_{20}H_2O_4S_6$ C, 46 31, H, 4 27 Found C, 45 92, H, 4 15

Preparation of **20** by polymerization of 4,8-dihydro-1,3,5,7-tetrathia-1,2,3,5,6,7-hexahydro-2-indacyl-2,6-dithione hexanoate 1 30 g (2 5 mmol) of **19** in 50 mL of benzene and 5 mL of triethylphosphite were refluxed overnight to give a reddish-brown solid, softening point 122 °C. ^{13}C NMR 179 52, 169 47, 143.53, 127 22, 33 55, 31 16, 24 39, 22.27, 13 89 Calcd for $C_{20}H_{22}O_4S_4$ C, 52 84, H, 4 88, S, 28 21 Found C, 52 38, H, 4.65, S, 29 01

Preparation of the ditholium salt **21** from **16**. The dimethoxycarbonium pentachloroantimonate salt^5 was prepared by reaction of 4 24 g (20 mmol) of triethylorthoformate in 8 mL of CH_2Cl_2 at -78 °C with 29.8 g (50 mmol) of $SbCl_5$ in 8 mL CH_2Cl_2 The solution was warmed to rt and the white salt was recovered by filtration and washed with methylene chloride To a solution of 1 8 g (3 8 mmol) **16** in 90 mL of CH_2Cl_2 at -78 °C was added dropwise 1 12 g (3 0 mmol) of the dimethoxycarbonium ion salt in 60 mL of CH_2Cl_2 also cooled to -78 °C. The solution was stirred while warming to rt, filtered through $MgSO_4$, and allowed to slowly evaporate yielding 1 298 g (56% yield based on salt), mp 100 °C. ^{13}C NMR($CDCl_3$) 211 15(?), 170 53, 138 37, 127 51, 126 32, 123 71, 120 93, 33 79, 31 25, 24 63, 24 47, 22.27, 13 91

Preparation of the lithium salt **22**^{6} 0 22 g (0 28 mmol) of **21** was dissolved in 30 mL dry THF and cooled to 0°C. 0 2g $NaBH_4$ in dry THF was added in several portions and after 1 hr the mixture was allowed to warm to rt The solution was then cooled to -78°C and 0.2 mL (3 mmol, 1 5M)) of methyllithium was added, stirred and allowed to warm to rt. This solution was used directly in the next step

To the above solution was added 0 0528 g (0 10 mmol) of **19** The solution was stirred for 1 hr and 0 04 g (0 3 mmol) CH_3I was added and stirred for an additional 2 hr giving a light green solution The flask was placed in an ultrasonic bath for 1 hr at 70°C. A brown powder precipitated and was recovered by filtration, however, the NMR indicated incomplete removal of the SCH_3 groups and partial hydrolysis of the ester The sample was dissolved in 1,1,2,2-tetrachloroethane with a trace of p-toluene sulfonic acid and refluxed for several hours A dark reddish-brown material was isolated and then reacted with hexanyl chloride as described earlier yielding 40 mg of dark red-brown viscous oil, **24** ^{13}C NMR($CDCl_3$) 179 48, 171 04, 153 86, 138 59, 127 55, 127 32, 126 39, 123 54, 120 63, 110 12, 108 56, 34 57, 33 86, 31 19, 30 91, 29 41, 24 68, 24 36, 22 31, 13 97, 13 94

X-Ray Analysis. All X-ray data were collected on a R3M/μ update of a $P2_1$ diffractometer using the θ-2θ scan technique, variable scan rate, a graphite monochromator and Mo Kα radiation (λ = 71073 Å) Twenty five reflections were used in a least-squares refinement of unit cell parameters Lorentz-polarization and a Ψ-scan absorption correction were applied The structures were solved by direct methods and refined by a block-cascade least-squares technique. Compound 2. Space group $P\bar{1}$, a = 7.334(1), b = 8.193(1), c = 9 691(1) Å, α = 89 62(1), β = 83 68(1), γ = 64 31(1)°, V = 521 0(1) Å^3, Z = 2, D_{calcd} = 1 680 gcm^{-3}, μ = 6 60 cm^{-1}, R = 0 0569 for 1618 reflections and 162 parameters Compound 3. Space group $P\bar{1}$, a = 4 731(4), b = 7 809(7), c = 11 050(11) Å, α = 96 97(8), β = 94 96(8), γ = 98.78(7)°, V = 398.2(7) Å^3, Z = 1, D_{calcd} = 1.560 gcm^{-3}, μ = 3 43 cm^{-1}, R = 0 0562 for 1333 reflections and 134 parameters Compound 4. Space group $P\bar{1}$, a = 7 479(4), b = 12.331(6), c = 16.644(9) Å, α = 82.98(4), β = 86.64(4), γ = 80 43(4)°, V = 1501(1) Å^3, Z = 4, D_{calcd} = 1 520 gcm^{-3}, μ = 2.27 cm^{-1}, R = 0 0799 for 2395 reflections and 515 parameters Compound 5 Space group $P\bar{1}$, a = 9 363(10), b = 10 270(32), c = 11 076(35) Å, α = 96.65(26), β = 91 64(19), γ = 109 91(18)°, V = 1005(5) Å^3, Z = 2, D_{calcd} = 1 410 gcm^{-3}, μ = 4 61 cm^{-1}, R = 0 12 for 2205 reflections and 260 parameters. Compound 6a. Space group $P2_1/c$, a = 17 406(7), b = 20 741(7), c = 10 446(2) Å, β = 95 39(2)°, V = 3755(2) Å^3, Z = 4, D_{calcd} = 1 410 gcm^{-3}, R = 0 0861 for 3705 reflections and 455 parameters Compound 10. Space group $P\bar{1}$, a = 7 439(3), b = 8 188(3), c = 9 427(4) Å, α = 84 88(3), β = 77 80(3), γ = 63 81(3)°, V = 503 6(4) Å^3, Z = 2, D_{calcd} = 1 640 gcm^{-3}, μ = 4 91, R = 0 0566 for 1813 reflections and 161 parameters

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