Organic Metals. Systematic Molecular Modifications of Hexamethylenetetraheterofulvalene Donors

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Abstract: Two synthetic approaches for modifying hexamethylenetetraheterofulvalene donors are described for the purpose of perturbing in a systematic way the interesting solid state properties of the TCNQ salts of the parent systems. The first approach consists of a steric modification in which a methyl group is introduced into the outer five-membered rings of the parent molecules to give di(3-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetrathiafulvalene (**6a**, α-MeHMTTF), di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetrathiafulvalene (**6b**, β-MeHMTTF), di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,5- (and/ or 1,8-)diselena-4,8- (and/or 4,5-)dithiafulvalene (**11**, β-MeHMDSeDTF) and di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetraselenafulvalene (**9**, β-MeHMTSeF). Donor **6b** forms both insulating and highly conducting (σ_{RT} = 80/ohm·cm, single crystal) charge transfer complexes with TCNQ, whereas the selenium-containing analogues, **11** and **9**, form only insulating TCNQ compounds. Donor **6a** gives a moderately conducting TCNQ complex (σ_{RT} = 10^{-1}/ohm·cm). The second type of modification involves an electronic perturbation in which the outer five-membered alkyl rings are replaced with fused thiophene derivatives to give *cis-/trans*-dithieno[2,3-*b*;2′,3′-*h*]-1,4,5,8-tetrathiafulvalene (**26**, α-TTTF) and the separable cis and trans isomers of di(4,5-dihydrothieno)-[2,3-*b*;2′,3′-*h*]-1,4,5,8-tetrathiafulvalene (**24a**, *cis-*, and **24b**, *trans*-α-DTTTF). Both **24a** and **24b** form highly conducting TCNQ complexes (σ_{RT} ≈ 20/ohm·cm, powder) whereas **26** forms a semiconducting TCNQ complex.

Since the discovery of unusual metal-like conductivity in the organic charge-transfer complex, tetrathiafulvalene-tetracyano-*p*-quinodimethane (TTF-TCNQ, **1a–2**),[2a] numerous new derivatives have appeared.[2b,3] The most successful modifications of TTF, in terms of the solid state properties of the resulting TCNQ complexes, have involved replacement of the sulfur atoms with selenium (e.g., TSeF[4] (**1b**) and *cis-/trans*-DSeDTF[5] (**1c**)),[6] addition of electron-donating substituents (e.g., alkyl groups),[7–9] and combinations of both these modifications.[10–14]

A focal point for a large part of the research on TTF-TCNQ has centered on trying to gain a better understanding of the metal-insulator phase transition which turns off the high conductivity at low temperature (T_c = 53 K).[15] An eventual goal is to prepare a ground-state metal, i.e., a material in which
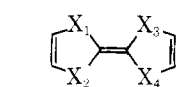
1a, X_{1-4} = S
b, X_{1-4} = Se
c, $X_{1,3}$ = S, $X_{2,4}$ = Se;
      $X_{1,4}$ = S, $X_{2,3}$ = Se

2
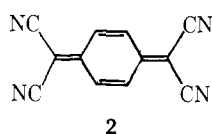
the phase transition is completely absent.[16] In general, this phase transition derives from the quasi-one-dimensional character of the segregated donor and acceptor stacked structure found in these materials which makes them susceptible to lattice distortions which open an energy gap in the conduction band.[15]

Selenium substitution of the sulfur atoms in TTF was found to stabilize the phase transition to lower temperatures (e.g., DSeDTF-TCNQ, T_c = 44 K, and TSeF-TCNQ, T_c = 28 K).[17] A major factor considered to be responsible for this lowering is stronger electronic overlap between the donor and acceptor stacks.[17,18]

Recently, an alkyl derivative of TSeF, hexamethylene-TSeF (HMTSeF, **3a**), was found to form a TCNQ salt which undergoes a very broad maximum in conductivity with de-

creasing temperature and which maintains considerable conductivity at very low temperature.[13] HMTSeF-TCNQ adopts a crystal structure[19] which is more close packed than TTF-TCNQ with shorter interstack distances, and this feature may be responsible for the unusual low-temperature behavior of this material.

Even more interesting was the observation that with the application of pressure,[20] the broad conductivity maximum vanishes completely and the solid behaves like a semimetal, where apparently the phase transition has been completely suppressed. Subsequently, the structurally related sulfur analogue, HMTTF-TCNQ[9] (HMTTF: hexamethylene-TTF, **3b**), which is normally insulating at low temperatures (below T_c), was found to display similar behavior. Pressure converts the low-temperature insulating state to a metallic phase.[21]

In order to probe the molecular features responsible for these interesting low-temperature properties of HMTTF-TCNQ and HMTSeF-TCNQ, we have carried out some systematic chemical modifications on these donors. Two basic types of modifications have been pursued. The first involves a steric perturbation in which one methyl group is incorporated into
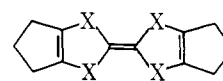

3a, X = Se
b, X = S

each of the fused five-membered alkyl rings. This should serve mainly to alter crystal packing of the charge-transfer complex while having minimal effect on the electronic properties of the donor. The second type of modification involves an electronic alteration in which the heterofulvalene π framework has been extended by incorporating a sulfur in place of an α-methylene group.[22] Not only is this modification expected to perturb the electronic properties of the donor, but the added sulfur atoms are in positions where they could contribute to the overlap with the acceptor, assuming that the crystal packing of the congeners (HMTTF-TCNQ and HMTSeF-TCNQ) is only slightly altered.

Steric Modification. While a variety of synthetic routes are available for preparing TTF derivatives,[2b] we choose to ex-

Scheme I
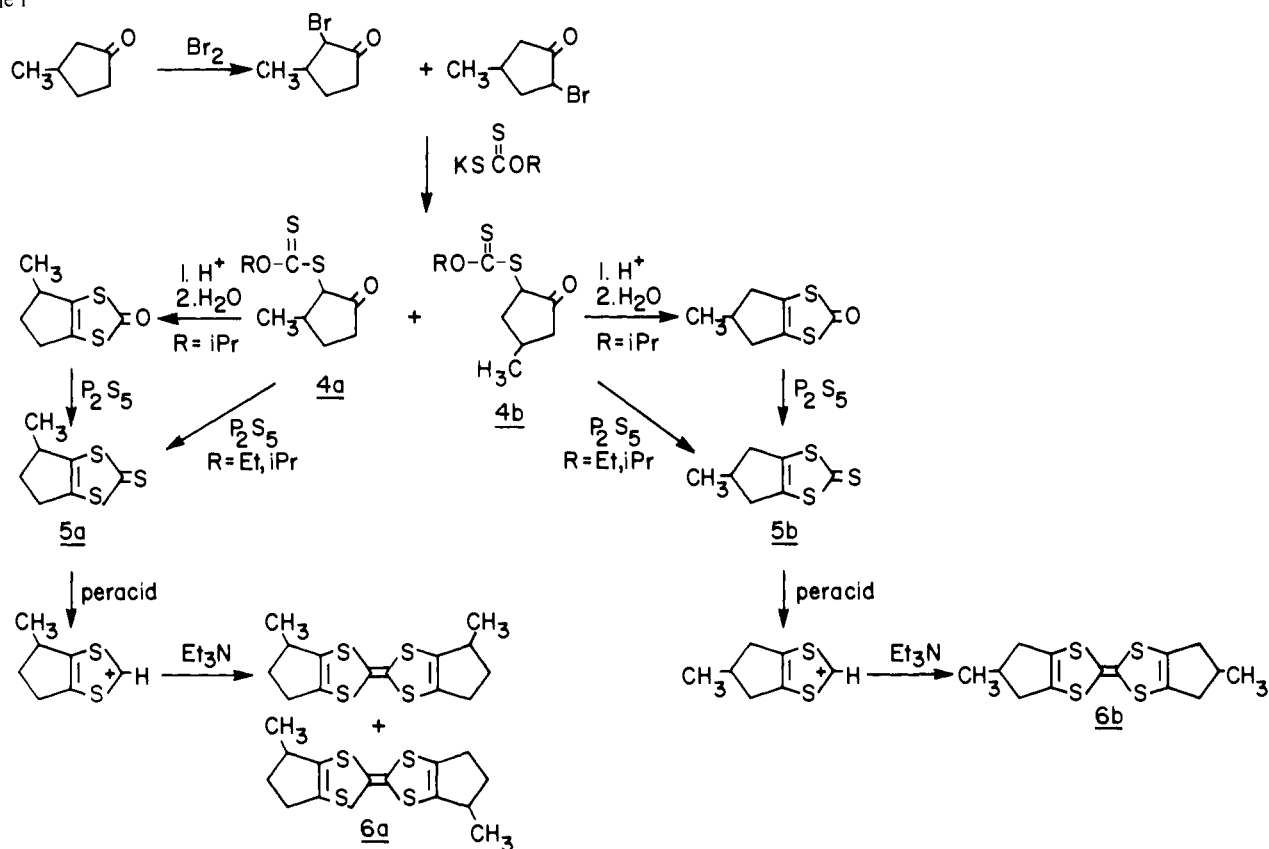
Table I. ^{13}C NMR Chemical Shifts (CHCl₃, δ)

Assign-	Compd			
ment	5a	5b	7b	8b
Methyl	20.9	21.5	21.4	21.3
Methine	30.4	36.4	35.8	36.7
Methylene	35.4	39.0 (2 C)	39.4	41.3 (2 C)
Methylene	39.3		41.4	
Vinyl	141.4	141.6 (2 C)	142.1	150.7 (2 C)
Vinyl	148.4		144.1	
Carbonyl	218.3	220.0	221.1	194.0

amine two procedures that appeared suitable for sterically modifying HMTTF and its selenium analogues. The first procedure is outlined in Scheme I and is an improved modification of our initial route to HMTTF.[9,23] Bromination of 3-methylcyclopentanone afforded a mixture rich in the 2- and 5-monobrominated isomers. Treatment of this bromide mixture with potassium isopropyl xanthate yielded the corresponding oxo xanthates (**4a** and **4b**) which could be separated by careful column chromatography. Acid-induced cyclization[24] of these individual xanthates provided the corresponding dithiocarbonates which were subsequently converted into 3- and 4-methylcyclopenteno[1,2-d]-1,3-dithiole-2-thiones (**5a** and **5b**) on treatment with P₂S₅. As expected, the ^{13}C NMR spectrum of **5a** exhibited a seven-line pattern, whereas the more symmetrical **5b** gave only five resonances (see Table I).

An alternate, lower yield route[9] to **5b** involved ring closure of the mixture of oxo xanthates **4a** and **4b** with P₂S₅ to give a mixture of thiones **5a** and **5b**. Crystallization from hexane provided only the 4 isomer (**5b**).
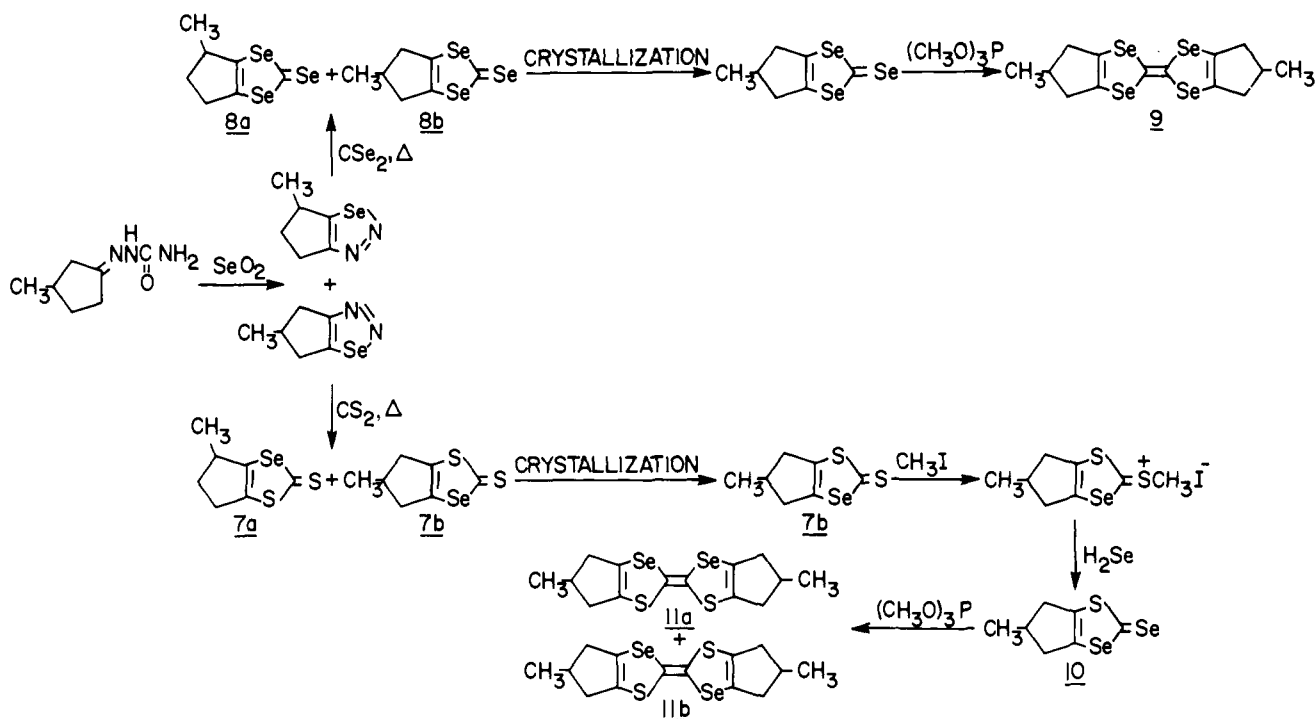
Coupling of **5a** and **5b** was accomplished in an analogous fashion as for TTF.[25] Peracid oxidation of **5a** and **5b** gave the corresponding 1,3-dithiolium salts,[26] which were treated with triethylamine to yield di(3-methylcyclopenteno)-[1,2-b;1',2'-h]-1,4,5,8-tetrathiafulvalene (**6a**, α-MeHMTTF) and

di(4-methylcyclopenteno)-[1,2-b;1',2'-h]-1,4,5,8-tetrathiafulvalene[27] (**6b**, β-MeHMTTF), respectively. The α-methyl isomer **6a** on recrystallization yielded yellow microcrystals melting at 137–139 °C from hexane and 119–120 °C from nitroethane. Both high- and low-melting forms had identical spectroscopic properties but formed different TCNQ charge transfer salts (see later). Although four possible geometrical isomers are possible, no attempt was made to distinguish between them.
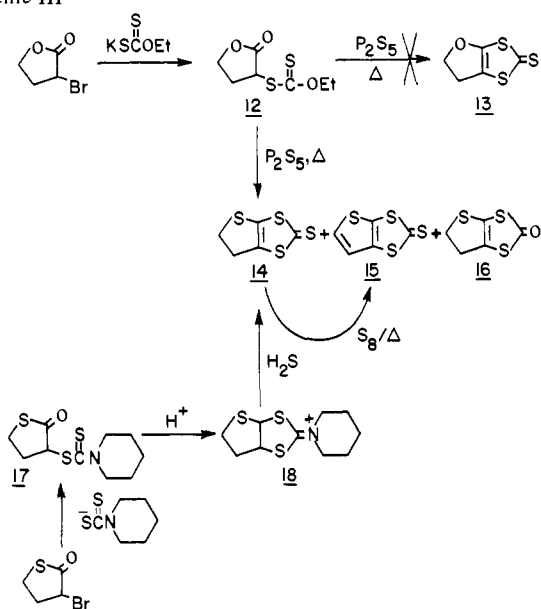
Intermediates **5a** and **5b** can also be prepared by a recently developed route involving thermal decomposition of substituted 1,2,3-thiadiazoles in the presence of carbon disulfide.[23b] This procedure has been extended to selenium-containing species by decomposition of 1,2,3-selenadiazoles[28] in the presence of carbon disulfide[11] or carbon diselenide.[14]

The selenadiazole route provided a convenient means of preparing the selenium analogues of β-MeHMTTF. Treatment of the semicarbazone of 3-methylcyclopentanone with selenium dioxide effects ring closure to the corresponding 1,2,3-selenadiazole.[28] Cyclization appears to occur at both α-methylene positions to give a mixture of 3- and 4-methyl isomers as judged by two close peaks in the liquid chromatogram of the product and by an apparent triplet for the methyl absorption in the ^{1}H NMR (i.e., two overlapping doublets). Thermal decomposition of this selenadiazole mixture in the presence of either carbon disulfide or carbon diselenide provides the expected 1,3-thiaselenole-2-thione (**7a** and **7b**) and 1,3-diselenole-2-selone (**8a** and **8b**) derivatives, respectively. Here also, liquid chromatography and ^{1}H NMR suggested a mixture of 3 and 4 isomers; however, on crystallization from hexane only one pure isomer was obtained. The identity of the isomer **8b** was readily determined from ^{13}C NMR which showed only five signals, consistent with the assignment of the methyl in the 4 position (Table I). While the lower symmetry of **7b** does not permit an easy distinction from isomer **7a**, based on our experimental results for **6b** and **8b**, and on a comparison

Scheme II

CH₃ ... **8a** + CH₃ ... **8b** → CRYSTALLIZATION → CH₃ ... $\xrightarrow{(CH_3O)_3P}$ CH₃ ... CH₃ **9**

$\uparrow$ CSe₂, Δ

CH₃ ... (hydrazide) $\xrightarrow{SeO_2}$ +

CH₃ ...

$\downarrow$ CS₂, Δ

CH₃ ... **7a** + CH₃ ... **7b** → CRYSTALLIZATION → CH₃ ... **7b** $\xrightarrow{CH_3I}$ CH₃ ... SCH₃ I⁻

$\downarrow$ H₂Se

CH₃ ... **11a** +

CH₃ ... **11b**

$\xleftarrow{(CH_3O)_3P}$ CH₃ ... **10**

Scheme III

$\xrightarrow{KS\overset{S}{\underset{\parallel}{C}OEt}}$ **12** $\xrightarrow[\Delta]{P_2S_5}$ **13**

$\downarrow P_2S_5, \Delta$

14 + **15** + **16**

$\uparrow H_2S$ ... S_8/Δ

17 $\xrightarrow{H^+}$ **18**

$\uparrow \overset{S}{\underset{\parallel}{SCN}}$

... Br

of the chemical shifts in Table I, crystallization here also has apparently selected for the 4-methyl isomer.

The coupling procedure described for **5b** is not successful with the selenium analogues **7b** and **8b**.[4,5,17a] However, in the case of **8b**, the presence of the selone group permits smooth conversion to di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetraselenafulvalene (**9**, β-MeHMTSeF) on treatment with trimethyl phosphite in refluxing benzene. The less reactive thiones **5b** and **7b** couple under more strenuous reaction conditions and in lower yields (~5%).[29] In the case of **7b**, the possibility of sulfur-selenium scrambling[30] necessitates the conversion of the thione into the more reactive selone **10**. This is readily accomplished by treatment with methyl iodide and reaction of the resulting methiodide with hydrogen selenide.[31] Treatment of **10** with trimethyl phosphite gave di(4-methyl-cyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,5- (and/or 1,8-)diselena-4,8-

(and/or 4,5-)dithiafulvalene (**11a**, cis; **11b**, trans; β-MeHMDSeDTF), probably as a mixture of *cis*- and *trans*-DSeDTF isomers.[32] Scheme II summarizes the reactions leading to donors **9** and **11**.

In donors **6b**, **9**, and **11**, the β-methyl groups can be either syn or anti relative to the molecular plane. While both isomers are probably formed on coupling, we have not tried to distinguish between them.[33]

Electronic Modification. As described earlier, we planned to electronically modify the hexamethylenetetraheterofulvalene donor system by replacing an α-methylene group with a chalcogen. We found that commercially available α-bromo-γ-butyrolactone underwent nucleophilic displacement with potassium ethyl xanthate to give the oxo xanthate ester **12**. Cyclization of **12** with P₄S₁₀ in refluxing decalin[34] did not afford the expected dithiole derivative **13**, but 4,5-dihydro-thieno[2,3-*d*]-1,3-dithiole-2-thione (**14**) as the major product,[35] as well as smaller amounts of thieno[2,3-*d*]-1,3-dithiole-2-thione (**15**) and 4,5-dihydrothieno[2,3-*d*]-1,3-dithiol-2-one (**16**). Product **14** could also be obtained from the reaction of α-bromo-γ-thiobutyrolactone with piperidinium *N,N*-pentamethylenedithiocarbamate to give the oxo ester **17**, followed by acid-catalyzed cyclization to the iminium salt **18**.[34a,36] Treatment of **18** with hydrogen sulfide provided the thione **14**. Scheme III outlines these reactions. The dihydro-thieno derivative **14** can be converted to **15** by sulfur dehydrogenation at 180 °C. Treatment of **14** with mercuric oxide in acetic anhydride gave **16**.

Attempts to prepare the oxygen analogue of **18** have so far been unsuccessful. While treatment of α-bromo-γ-butyro-lactone with piperidinium *N,N*-pentamethylenedithiocarba-mate gave the expected oxo xanthate ester **19**, this material could not be cyclized with acid to the corresponding iminium salt **20** (Scheme IV).

Extension of some of this chemistry to selenium analogues was attempted by treating α-bromo-γ-thiobutyrolactone with piperidinium *N,N*-pentamethylenediselenocarbamate[37] to give **21**. Cyclization of **21** with acid apparently gives the iminium salt **22** based on NMR data, but in very low yield (Scheme V). Because of the low yields and reduced stability of these sele-
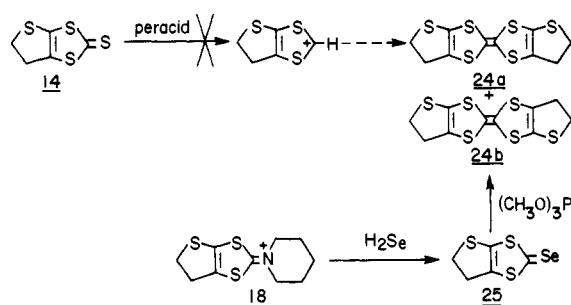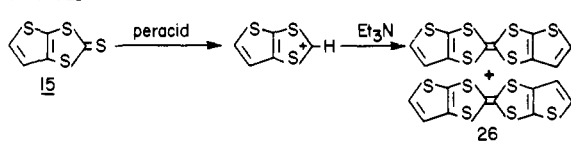
Scheme IV
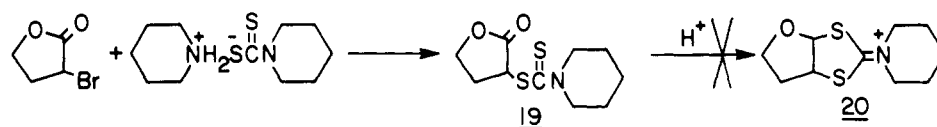
Scheme V
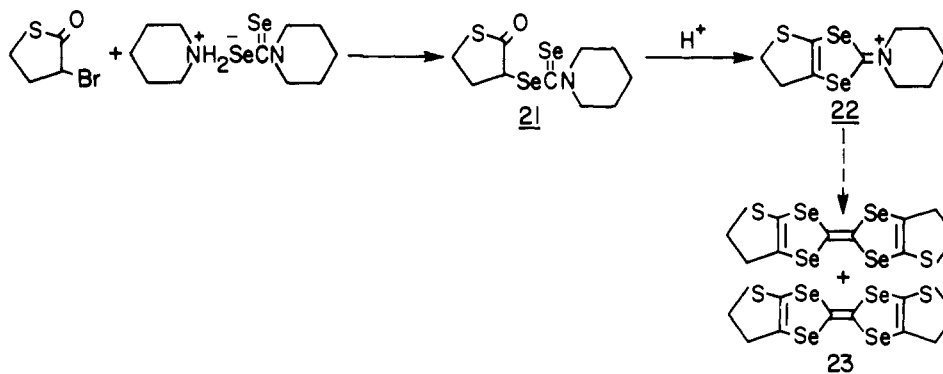
Scheme VI

Scheme VII

nium intermediates, we have not as yet converted **22** to di(4,5-dihydrothieno)-[2,3-*b*;2',3'-*h*]-1,4,5,8-tetraselenafulvalene (α-DTTSeF, **23**).

Attempts to couple **14** to di(4,5-dihydrothieno)-[2,3-*b*; 2',3'-*h*]-1,4,5,8-tetrathiafulvalene (**24**, α-DTTTF) by the usual procedure of peracid oxidation, followed by base coupling, were not successful. However, **24** could be prepared by treatment of iminium salt **18** with hydrogen selenide to give the selone derivative **25**, which readily couples on treatment with trimethyl phosphite in refluxing benzene (Scheme VI). **15**, on the other hand, can be converted to dithieno[2,3-*b*;2',3'-*h*]-1,4,5,8-tetrathiafulvalene (**26**, α-TTTF) (probably a mixture of cis and trans isomers) by reaction with *m*-chloroperbenzoic acid to give the corresponding dithiolium salt which can be subsequently coupled with triethylamine (Scheme VII).

Interestingly, the solubility differences between the cis and trans isomers of **24** permit facile separation of these two materials. Trimethyl phosphite coupling of selone **24** in a concentrated benzene solution precipitated a dark brown solid. Workup of the remaining reaction mixture by chromatography provided a red solid. The dark brown and red solids gave identical elemental analyses and mass spectra consistent with their being isomers of the expected product **24**. Similar spectroscopic and electrochemical data were also found (see Table II). Based on its poor solubility characteristics and higher

melting point, we have assigned the brown solid as the trans isomer (**24b**); the more soluble red solid is assigned as the cis isomer (**24a**).

TCNQ Charge Transfer Complexes. Table II summarizes some data on sterically (**6a**, **6b**, **9**, and **11**) and electronically (**24a**, **24b**, and **26**) modified hexamethylenetetraheterofulvalene donors, along with data on parent systems **3a** and **3b**. The data support the contention that the steric modification has left electronic properties of the parent donor system relatively unperturbed. The electronic modifications have lead to slightly poorer donors relative to HMTTF, as judged by the cyclic voltammetry data.

The poor solubility of HMTTF and HMTSeF makes purification and crystal growth of their charge transfer complexes very difficult. In this regard, the lower symmetry of the methyl derivatives (**6**, **9**, and **11**) leads to considerably improved solubility characteristics.

It was hoped that the methyl derivatives would alter the crystal packing of their TCNQ complexes, without seriously affecting the close stacking of the donors. Apparently, this steric modification is on the borderline of stability for the conducting phase. Reaction of β-MeHMTTF with TCNQ led to the formation of both insulating and highly conducting charge transfer compounds, while β-MeHMDSeDTF and β-MeHMTSeF provided only insulating TCNQ complexes. The insulating phases analyze as 2:1 donor–acceptor complexes while the conducting phase of β-MeHMTTF-TCNQ was a 1:1 complex. The high-melting form (137–139 °C) of α-MeHMTTF gave a moderately conducting TCNQ compound (see Table II), while the low-melting form (119–120 °C) provided only an insulating TCNQ complex. Both complexes had 1:1 stoichiometries.

The electronic spectrum of TCNQ charge transfer compounds in KBr is very characteristic of the particular type of stacking arrangement.[38] In general for simple 1:1 organic charge transfer salts, the highly conducting systems have a broad, intense absorption ≥ 2.0 μ. This is believed to be a mixed valence transition and indicative of the segregated stacked structure which is required for high conductivity. On the other hand, poorly conducting materials display absorptions around 1.0 μ. These absorptions are typical of charge transfer transitions in an alternating donor–acceptor stacking arrangement (i.e., the D–A structure) in the solid; however, other crystal packing arrangements are possible (e.g., dimeric stacking arrangements) which may have absorptions near 1.0 μ.

Consistent with its high conductivity, β-MeHMTTF–

Table II. Data on Hexamethylenetetraheterofulvalene Derivatives

Property	HMTTF (3b)	HMTSeF (3a)	cis-α-DTTTF (24a)	trans-α-DTTTF (24b)	α-TTTF (26)	α-Me-HMTTF (6a)	β-Me-HMTTF (6b)	β-MeHM-DSeDTF (11)	β-MeHM-TSeF (9)
Electronic spectrum	465 (2.53)	493 (2.36)	476 (2.68)	483 (2.81)		465 (2.70)	468 (2.60)	475 (2.20)	498 (2.32)
λ (log ε), nm		350 (sh)	370 (sh)	370 (sh)		330 (sh)	330 (sh)	340 (sh)	350 (sh)
(PhCl)	315 (4.09)	303 (4.22)	340 (sh)	340 (sh)		313 (4.22)	315 (4.14)	310 (4.15)	303 (4.21)
			323 (4.30)	323 (4.10)					
		310 (sh)	310 (sh)						
Cyclic voltammetry[a]									
$\epsilon_{1/2}$, V	0.33	(0.44)[b]	0.43	0.43	0.47	0.30	0.30	0.39	0.48
ϵ_p, V	0.66	(0.72)[b]	0.69	0.69	0.74	0.64	0.63	0.70	0.75
TCNQ salt data									
stoichiometry (D:A)	1:1	1:1	1:1	1:1	1:1	1:1 [e,f]	1:1 [g] / 2:1 [h]	2:1	2:1
Mp, °C			185 dec	185 dec	~260 dec	139-140[e] / 134-135[f]	186[g] / 187-188[h]	200-201	215-220 dec
Conductivity, (ohm cm)$^{-1}$	5[c] / 500[d]	50[c] / 2000[d]	30[c]	30[c]	10^{-3d}	$10^{-1 d,e}$ / $10^{-6 d,f}$	80[d,g] / $10^{-8 c,h}$	10^{-8c}	10^{-8c}
Electronic spectrum μ (KBr)	~2.3	>2.5	>2.5	>2.5	1.3	>2.5[e] / 0.6[f]	~2.4[g] / 0.6[h]	0.6	0.6

[a] Peak potentials vs. SCE in CH_3CN, 0.1 N TEAP. [b] Data for tetramethyl-TSeF since HMTSeF is too insoluble in CH_3CN for measurement. Both tetramethyl-TSeF and HMTSeF gave similar oxidation potentials in CH_2Cl_2: 0.55, 0.94 eV. [c] Compaction measurement. [d] Single crystal measurement. [e] High mp donor fraction, 137–139 °C; see text. [f] Low mp donor fraction, 119–120 °C; see text. [g] Black phase; see text. [h] Green phase; see text.

TCNQ has a broad, intense absorption in the infrared (Table II), typical of the segregated uniform stacked structure of TTF-TCNQ. The insulating TCNQ salts of **6a, 6b, 9,** and **11** lack this absorption and instead display a broad absorption at 0.6 μ.

Both cis and trans isomers of α-DTTTF form 1:1 highly conducting, isostructural TCNQ salts with broad absorptions extending to >2.5 μ (Table II). In contrast, the related α-TTTF donor forms a 1:1 semiconducting TCNQ salt with an absorption at 1.3 μ which suggest a nonuniform stacking of the constituents or an alternating donor–acceptor stacked structure.

Initial attempts to obtain single crystals of the conducting TCNQ salts of *cis-* and *trans-*α-DTTTF have so far been unsuccessful. We have therefore included compaction conductivity data on HMTTF-TCNQ and HMTSeF-TCNQ in Table II for comparison with the results on these new donors.

It is interesting to note the large decrease in conductivity in going from *cis-* or *trans-*α-DTTTF-TCNQ to α-TTTF-TCNQ since both steric and electronic (i.e., cyclic voltammetry data) properties are very similar for these donors. While the reasons for this behavior are not clear at present, a possible explanation may involve changes in the association equilibria in solution due to the presence of an additional site for acceptor complexation in α-TTTF (**26**). TCNQ is known to form weak charge-transfer complexes with aromatic donors in solution.[39] Such complex formation of TCNQ with the thiophene portion of α-TTTF may modify solution equilibria so that a D-A structure is favored over the segregated stacked structure. The poorly conducting properties of the mono-[40] and dibenzo-[41] TTF-TCNQ salts may also be understood in these terms. Bearing on this point is a recent crystal structure determination[42] on a dibenzo TTF-TCNQ derivative which shows the TCNQ located over the benzene portion of the donor in a D-A stacking arrangement.

We are currently pursuing a detailed study of the solid state properties of these TCNQ complexes.

Experimental Section

3- and 4-Methylcyclopenteno[1,2-*d*]-1,3-dithiole-2-thione (5a and 5b). To a stirred solution of 17.6 g of 3-methylcyclopentanone in 20 mL of chloroform was added dropwise 9.5 mL of bromine. Immedi-

ately after this addition, the product mixture was flash-distilled under vacuum to yield a principal fraction (>80 °C, 1 Torr) of 17 g of the colorless α-brominated products. The distillation flask must not be allowed to go dry as extensive decomposition may occur on overheating. The mixture of bromides was then added dropwise to an ice-cooled slurry of 17.4 g of potassium isopropyl xanthate in acetone (200 mL). After stirring cold for 1 h, the solution was filtered and the acetone removed under vacuum to yield an oil. This oil was then dissolved in hexane and filtered and the hexane was removed to give a light yellow oil which exhibited three spots on TLC. The dark central spot was further resolved by column chromatography (1-m silica gel column, 5% ether–hexane) into colorless oils of 3- and 4-methyl-2-isopropylxanthylcyclopentanone (**4a** and **4b**, respectively (yields: 30 and 37%)). The 4-methyl isomer, **4b**, eluted first.

4a: IR (film) 2963 (s), 1758 (s), 1465 (m), 1380 (m), 1250 (s), 1146 (m), 1090 (s), 1037 (s), 902 (m), 875 cm^{-1} (m); NMR (CDCl₃) δ 5.65 (1 H, heptet, J = 6 Hz), 3.62 (1 H, doublet, J = 10 Hz), 2.59–1.49 (5 H, multiplet), 1.36 (6 H, doublet, J = 6 Hz), 1.22 and 1.01 (3 H, two doublets (cis and trans methyl), J = 6 Hz).

4b: IR (film) 2963 (s), 1752 (s), 1459 (m), 1379 (m), 1243 (s), 1147 (m), 1090 (s), 1037 (s), 902 cm^{-1} (m); NMR (CDCl₃) δ 5.64 (1 H, heptet, J = 6 Hz), 4.32–3.96 (1 H, multiplet), 2.80–1.56 (5 H, multiplet), 1.33 (6 H, doublet, J = 6 Hz), 1.15 and 1.13 (3 H, two doublets (cis and trans methyl), J = 6 Hz).

The respective xanthate esters **4a** and **4b** (2.0 g) were cyclized by slow addition to 10 mL of concentrated H_2SO_4 at 0 °C, stirring for 0.5 h, and pouring the solution over ice and extraction with ether to give the expected α- and β-methyl dithiocarbonates.

3-Methylcyclopenteno[1,2-*d*]-1,3-dithiol-2-one: colorless oil; IR (film) 2968 (s), 2932, 2870 (m), 1718 (s), 1672 (vs), 1626 (m), 1586 (m), 1458 (m), 1380 (w), 1332 (w), 1222 (w), 912 (s), 800 (m), 735 cm^{-1} (s); NMR (CDCl₃) δ 3.35–3.00 (1 H, multiplet), 2.88–2.68 (1 H, multiplet), 2.68–2.25 (2 H, multiplet), 1.94–1.54 (1 H, multiplet), 1.17 (3 H, doublet, 6 J = Hz).

4-Methylcyclopenteno[1,2-*d*]-1,3-dithiol-2-one: colorless oil; IR (film) 2963 (s), 2932, 2857 (m), 1720 (s), 1678 (vs), 1618 (s), 1584 (m), 1450 (m), 1382 (w), 1273 (w), 960 (w), 910 (m), 813 cm^{-1} (m); NMR (CDCl₃) δ 3.15–2.52 (3 H, multiplet), 2.34 (2 H, doubled doublet, J = 4 and 12 Hz), 1.18 (3 H, doublet, J = 6 Hz).

Normally, the crude dithiocarbonate products were converted directly into trithiocarbonates (**5a** and **5b**) by treatment with excess P_2S_5 in boiling decalin for 0.5 h. The yield for the two-step conversion from **4a** and **4b** to **5a** and **5b** was 80%. Column chromatography (silica gel, hexane) afforded the pure materials.

5a: yellow oil; IR (film), 2959 (s), 2924 (m), 2860 (m), 1563 (w), 1453 (m), 1378 (w), 1328 (w), 1300 (w), 1117 (m), 1056 (s, thiocarbonyl), 1000 (m), 903 (w), 838 cm^{-1} (w); NMR (CDCl₃) δ

3.35–3.00 (1 H, multiplet), 2.88–2.40 (3 H, multiplet), 2.15–1.75 (1 H, multiplet), 1.20 (3 H, doublet, $J = 7$ Hz); see Table I for ^{13}C NMR.

5b: bright yellow needles; mp 60–61 °C; IR (KBr) 2960 (w), 1443 (m), 1382 (m), 1108 (m), 1050 (s), 842 cm^{-1} (m); NMR (CDCl$_3$) δ 3.10–2.70 (3 H, multiplet), 2.60–1.10 (2 H, multiplet), 1.21 (3 H, doublet, $J = 6$ Hz); see Table I for ^{13}C NMR.

Di(3-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetrathiafulvalene (6a). To a stirred, 0 °C suspension of **5a** (131 mg, 0.7 mmol) in acetone was added dropwise a solution of *m*-chloroperbenzoic acid (480 mg, 2.8 mmol) in acetone (10 mL). The slightly orange solution was stirred at 0 °C for 20 min. Then perchloric acid (70%, 2.8 mL) was added dropwise and the mixture stirred for 0.5 h. Anhydrous ether (1 L) was added and the cloudy solution was cooled in a freezer (−15 °C) overnight. The white perchlorate (*caution:* 1,3-dithiolium perchlorates are known to explode violently)[43,44] was filtered, but *not allowed to become dry*, and immediately washed into a flask with acetonitrile (ca. 25 mL). Triethylamine was added and the solution turned dark orange. The solvent was evaporated and the remaining oil extracted with hot hexane from which crystallized yellow crystals of **6a** in two crops melting at 119–120 °C from nitroethane and at 137–139 °C from hexane (combined yield 37%): NMR (CDCl$_3$) δ 3.10–2.78 (2 H, multiplet), 2.70–2.35 (6 H, multiplet), 2.05–1.80 (2 H, multiplet), 1.10 (6 H, doublet, $J = 6$ Hz); mass spectrum mol wt calcd 312.013, found 312.016; see Table II for UV–vis and electrochemical data.

Di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetrathiafulvalene (6b). The same procedure as described for the preparation of **6a** was employed to couple **5b** to **6b**. The product crystallized from hexane as bright yellow needles (yield 32%): mp 155–156 °C; NMR (CDCl$_3$) δ 3.00–2.40 (6 H, multiplet), 2.30–1.80 (4 H, multiplet), 1.16 (6 H, doublet, $J = 6$ Hz); mass spectrum mol wt calcd 312.013, found 312.018; see Table II for UV–vis and electrochemical data.

4-Methylcyclopenteno[1,2-*d*]-1,3-thiaselenole-2-thione (7b). To a mechanically stirred solution of 50 g of 3-methylcyclopentanone semicarbazone (0.3 mol) in 400 mL of glacial acetic acid at ∼5 °C was added 72 g of finely powdered selenium dioxide in small portions. After addition was complete, the ice bath was removed and the reaction mixture stirred at room temperature for 3 h. The dark reaction mixture was filtered and water was added to the filtrate and then extracted with chloroform. The chloroform extracts were washed with water and saturated NaHCO$_3$ and dried (MgSO$_4$), and the solvent was evaporated to give a red-brown oil. This oil was dissolved in benzene and placed on a column (400 g, Silicar CC-7) and eluted with benzene. The first yellow fraction (∼2 L of benzene) was evaporated to give 35 g of the 1,2,3-selenadiazole as a yellow-orange oil. The selenadiazole consists of approximately equal amounts of the α- and β-methyl isomers ad judged by HPLC (μ-porasil, isooctane) and by NMR which displayed an apparent triplet for the methyl absorption as a result of two overlapping doublets: NMR (benzene) δ 3.4–1.8 (5 H, multiplet), 1.0 (3 H, triplet).

The selenadiazole was mixed with 80 mL of carbon disulfide and kept at 140 °C for 3 h in a bomb. The excess CS$_2$ was removed from the reaction mixture, and the resulting black oil chromatographed (silica gel), eluting with 3:1 hexane–chloroform to give a red oil. Extraction with hot hexane gave on cooling orange crystals of 4-methylcyclopenteno[1,2-*b*]-1,3-thiaselenole-2-thione (7b). The 3-methyl isomer (7a) is an oil and can be a problem in the crystallization of 7b. Apparently, only the 4-methyl isomer (7b) is obtained on crystallization as judged by its ^{13}C NMR spectrum, which shows chemical shifts consistent with this assignment and based on comparison with data on 5a, 5b, and 8b (see Table I). **7b:** mp 69–70 °C; IR (CCl$_4$) 1090, 1045 cm^{-1} (C=S); NMR (CDCl$_3$) δ 3.14–2.90 (3 H, multiplet), 2.55–2.35 (2 H, multiplet), 1.25 (3 H, doublet, $J = 7$ Hz); mass spectrum m/e 236 (based on ^{80}Se).

4-Methylcyclopenteno[1,2-*d*]-1,3-diselenole-2-selone (8b). The same procedure as described for the preparation of 7b was employed, except that 10 g of the selenadiazole was refluxed with 10 g of carbon diselenide[45] in toluene under N$_2$ for 1 h (*caution:* this procedure should be carried out in a well-ventilated hood; effluent should be passed through H$_2$O$_2$/KOH solutions to consume any excess CSe$_2$). The solvent is removed under reduced pressure and the resulting oil chromatographed (silica gel, 4:1 hexane–CHCl$_3$). A deep red intermediate fraction was collected and concentrated to a semisolid which was extracted with hot hexane to give 8b as red crystals in 10% yield: mp 103–105 °C; IR (CHCl$_3$) 910 (C=Se); NMR (CDCl$_3$) δ 3.2–2.2

(5 H, multiplet), 1.25 (3 H, doublet, $J = 6$ Hz); mass spectrum m/e 332 (based on ^{80}Se). The ^{13}C NMR spectrum of 8b exhibits five peaks (see Table I), which is consistent with the β-methyl assignment.

Di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,4,5,8-tetraselenafulvalene (9). To 0.33 g of 8b (1 mmol) in 25 mL of dry benzene under N$_2$ was added 0.3 g of freshly distilled trimethyl phosphite (2.4 mmol) and the solution refluxed for 5 h. The benzene was removed and the solution chromatographed (silica gel, 5–10% CHCl$_3$–hexane). The first orange band off the column was collected and concentrated to give **9** as an orange-red solid in 60% yield. Recrystallization from hexane gave orange-red prisms: mp 181–184 °C; NMR (CDCl$_3$) δ 3.20–2.00 (10 H, multiplet), 1.25 (6 H, doublet, $J = 7$ Hz); mass spectrum m/e 504 (based on ^{80}Se). See Table II for UV–vis and electrochemical data.

4-Methylcyclopenteno[1,2-*d*]-1,3-thiaselenole-2-selone (10). 7b (3.5 g, 15 mmol) and excess methyl iodide were refluxed in 50 mL of nitromethane for 4 h. After cooling to room temperature, 100 mL of hexane was added to the reaction mixture, then the mixture was filtered to give 3.0 g of the dark red methyl iodide salt. This material was dissolved in 70% MeOH and the solution was cooled to 0 °C under N$_2$. An excess of H$_2$Se (generated conveniently by treating Al$_2$Se$_3$ with H$_2$O) in a N$_2$ stream was bubbled through the stirred solution which turned bright red with precipitate formation. After 1 h, the reaction mixture was poured into water and extracted with ether. The ether was dried (MgSO$_4$) and evaporated to give **10** as a red solid in 40% yield. Recrystallization from hexane provided 10 as an orange-red solid: mp 85–86 °C; IR (CCl$_4$) 910 cm^{-1} (C=Se); NMR (CDCl$_3$) δ 3.22–2.20 (5 H, multiplet), 1.23 (3 H, doublet, $J = 6$ Hz); mass spectrum m/e 284 (based on ^{80}Se).

Di(4-methylcyclopenteno)-[1,2-*b*;1′,2′-*h*]-1,5- (and/or 1,8-)diselena-4,8- (and/or 4,5-)dithiafulvalene (11). Compound 7b was coupled to 11 as described in the preparation of 9. Recrystallization from hexane gave orange crystals: mp 160–163 °C; NMR (CDCl$_3$) δ 3.18–2.00 (10 H, multiplet), 1.27 (6 H, doublet, $J = 7$ Hz); mass spectrum m/e 408 (based on ^{80}Se). See Table II for UV–vis and electrochemical data.

4,5-Dihydrothieno[2,3-*d*]-1,3-dithiole-2-thione (14). To 48.1 g of potassium ethyl xanthate, suspended with stirring in 500 mL of acetone, was added 25 mL of α-bromo-γ-butyrolactone (Aldrich). After stirring for 0.5 h, the acetone was removed, the remaining oil was treated with ether, washed (three times, H$_2$O), and dried (MgSO$_4$), and the ether was removed to give the oxo xanthate ester 12 as a light yellow oil.

12: IR (film) 2984 (m), 2920 (m), 1780 (s), 1455 (m), 1377 (s), 1230 (s), 1205 (s), 1160 (s), 1117 (s), 1050 (s), 1025 (s), 1003 (s), 950 (m), 690 cm^{-1} (m); NMR (CDCl$_3$) δ 4.64 (2 H, quartet, $J = 7$ Hz), 4.60–4.25 (2 H, multiplet), 3.00–2.60 (1 H, multiplet), 2.60–2.20 (1 H, multiplet), 1.42 (3 H, triplet, $J = 7$ Hz), 1.60–1.22 (1 H, multiplet).

A solution of 12 (34.5 g) containing P$_2$S$_5$ (100 g) in decalin (700 mL) was heated to 150–160 °C with vigorous mechanical stirring for 0.5 h. After cooling, the dark orange solution was decanted and the residue extracted thoroughly with ether. The ether and decalin portions were combined and the ether was removed. The decalin solution was then run through a large chromatographic column (1.5 m, silica gel) with hexane elution. The bright yellow trithiocarbonate (14) is collected in low, variable yield (∼5–15%). 16 elutes first, followed by 15 and 14, respectively. Compound 14 can be converted to 15 on treatment with excess sulfur in decalin at 180 °C for 48 h (80% yield). Reaction of 14 with mercuric oxide in acetic anhydride provided 16.

14: yellow crystals; mp 110–111 °C; IR (KBr) 1500 (w), 1108 (m), 1035 (s, thiocarbonyl stretch), 988 cm^{-1} (s); NMR (CDCl$_3$) δ 3.74 (2 H, triplet, $J = 8$ Hz), 3.07 (2 H, triplet, $J = 8$ Hz); mass spectrum m/e 192.

15: red needles; mp 125–125.5 °C; IR (KBr) 1085 (m), 1063 (m), 1040 (s, thiocarbonyl stretch), 690 cm^{-1} (m); NMR (CDCl$_3$) δ 7.62 (1 H, doublet, $J = 5$ Hz), 7.02 (1 H, doublet, $J = 5$ Hz); mass spectrum m/e 190.

16: white needles; mp 84–85 °C; IR (KBr) 1625 (s, carbonyl stretch), 895 cm^{-1} (m); NMR (CDCl$_3$) δ 3.54 (2 H, triplet, $J = 8$ Hz), 3.08 (2 H, triplet, $J = 8$ Hz); mass spectrum m/e 176.

2 - (*N,N* - Pentamethyleneimino) - (4,5 - dihydrothieno[2,3 - *d*]) - 1,3 - dithiolium Tetrafluoroborate (18). α-Bromo-γ-thiobutyrolactone was prepared by a Hell–Volhard–Zelinskii type bromination[46] of γ-thiobutyrolactone (Aldrich). The material obtained after one dis-

tillation of the crude product was rather impure, but was used without further purification. α-Bromo-γ-thiobutyrolactone and an estimated excess of piperidinium *N,N*-pentamethylenedithiocarbamate were mixed in dry THF at room temperature. After 4 h, the reaction mixture was filtered and the solvent was evaporated. The resulting solid was recrystallized from heptane after treatment with Norit to give the intermediate oxo ester, (2 - oxodihydrothiopheno - 3 - yl) - *N,N*-pentamethylenedithiocarbamate (**17**), as off-white needles; mp 133–134 °C; NMR (CDCl₃) δ 5.28 (1 H, triplet, *J* = 9 Hz), 4.10 (4 H, broad singlet), 3.45 (2 H, multiplet), 3.2–2.0 (2 H, multiplet), 1.70 (6 H, broad singlet).

The oxo ester (20 mmol) was slowly dissolved in 10 mL of cold, concentrated H₂SO₄. Enough ethyl acetate to start precipitation of the hydrosulfate was cautiously added with stirring, and the resulting cloudy solution was poured into a cooled mixture of 60 mmol of HBF₄ (~54% in ether, Aldrich) in 180 mL of absolute EtOH. Addition of cold, dry ether gave **18** as slightly yellow crystals, mp 142–143 °C, in 50–55% yield: NMR (CDCl₃) δ 3.88 (6 H, broad singlet with fine structure), 3.35 (2 H, unsymmetrical triplet), 1.87 (6 H, broad singlet).

(2 - Oxodihydrofurano - 3 - yl) - *N,N* - pentamethylenedithiocarbamate (19). Equivalent amounts (~0.1 mol) of α-chloro-γ-butyrolactone and piperidinium *N,N*-pentamethylenedithiocarbamate were mixed in 500 mL of CH₂Cl₂ at room temperature. After 16 h, the reaction mixture was washed with H₂O (three times, 500 mL) and dried (MgSO₄), and the solvent was evaporated to give an off-white solid. Recrystallization from hexane/benzene/CHCl₃ (1:1:1) gave **19** in 95% yield as colorless crystals: mp 127–128 °C; NMR (CDCl₃) δ 5.20 (1 H, triplet, *J* = 9 Hz), ~4.5 (2 H, multiplet), 4.10 (4 H, broad singlet), ~3.3–2.0 (2 H, multiplet), 1.74 (6 H, broad singlet).

2 - (*N,N* - Pentamethyleneimino) - (4,5 - dihydrothieno[2,3 - *d*]) - 1,3 - diselenolium Tetrafluoroborate (22). The precursor to **22**, (2-oxodihydrothiophen-3-yl) *N,N*-pentamethylenediselenocarbamate (**21**), was prepared from piperidinium *N,N*-pentamethylenediselenocarbamate[37] as described for **18**, only at 0 °C. The product **21** crystallized from hexane-benzene (1:1) as yellow needles: mp 99–100 °C; NMR (CDCl₃) δ 5.08 (1 H, triplet, *J* = 9 Hz), 4.50 (2 H, multiplet), 3.94 (4 H, broad singlet), 3.5–2.1 (2 H, multiplet), 1.77 (6 H, broad singlet).

The ring closure of **21** proceeds as described for **16**, but in very low yield (<5%) to give **22** as an unstable, light brown solid: NMR (CDCl₃) δ 3.86 (6 H, broad singlet), 3.35 (2 H, triplet), 1.82 (6 H, broad singlet).

4,5 - Dihydrothieno[2,3 - *d*] - 1,3 - dithiole - 2 - selone (25). **18** (10 mmol) was reacted with excess H₂Se as described for the reaction of the methyl iodide salt of **7b** (see preparation of **10**). Recrystallization from heptane gave **25** as orange-red needles in 60% yield: mp 127–128 °C; IR (CHCl₃) 1505 (m), 1115 (m), 940 (s, C=Se stretch), 900 cm⁻¹ (m); NMR (CDCl₃) δ 3.83 (2 H, triplet, *J* = 8 Hz), 3.08 (2 H, triplet, *J* = 8 Hz); mass spectrum *m/e* 240 (based on ⁸⁰Se).

***cis-* and *trans-*Di(4,5-dihydrothieno)-[2,3-*b*;2′,3′-*h*]-1,4,5,8-tetrathiafulvalene (24a and 24b).** **25** (2 mmol) and 3 mmol of freshly distilled trimethyl phosphite were refluxed under N₂ in 10 mL of dry benzene for 5 h. The reaction mixture was allowed to cool to room temperature and was then filtered to give 120 mg of **24b** as a dark red, almost black powder, mp 195–196 °C (PhCl).

The solvent was evaporated from the filtrate and the remaining semisolid was purified by column chromatography (50 cm, silica gel). Elution started with hexane-CHCl₃ (9:1) and the polarity of the eluent was gradually increased to a 1:1 mixture of hexane-CHCl₃. The first yellow band was collected and the solvent evaporated to give 40 mg of **24a** as red crystals, mp 184–186 °C (CHCl₃).

Both **24a** and **24b** have identical infrared ((KBr), 2930, 2900, 2840, 1425, 1290, 1120, 1020 w, 765 m cm⁻¹) and mass spectra (*m/e* 320). The NMR spectrum of **24a** gave a similar splitting pattern as seen for **14** and **25** with the absorptions shifted slightly upfield as expected: NMR (CDCl₃) δ 3.77 (4 H, triplet, *J* = 8 Hz), 2.83 (4 H, triplet, *J* = 8 Hz).

Dithieno[2,3 - *b*;2′,3′ - *h*] - 1,4,5,8 - tetrathiafulvalene (26). The same procedure as described for the preparation of **6a** was employed to couple **15** to **26**. The product was crystallized from hexane as yellow needles in 30% yield: mp 214–215 °C dec; NMR (CDCl₃) δ 6.82 (2 H, doublet, *J* = 5 Hz), 7.24 (2 H, doublet, *J* = 5 Hz); mass spectrum *m/e* 316.

Preparation of TCNQ Charge Transfer Salts. The typical procedure for preparing charge transfer salts of the new donors involved mixing

of equal molar amounts of solutions of the donor and of TCNQ. The charge transfer salt usually precipitates out immediately; however, cooling was sometimes necessary. For donors **6a, 6b, 11, 9,** and **24a,** acetonitrile or nitroethane was employed as a solvent. The less soluble **24b** was dissolved in hot chlorobenzene.

The techniques[47] employed in trying to obtain single crystals of these charge transfer salts involved slow cooling from saturated solutions, diffusion, and solvent evaporation. Crystals large enough for four probe dc conductivity measurements[48] were obtained only for **6a, 6b,** and **26.** In the case of **6b,** insulating (green rods) and conducting (black needles) phases were obtained depending in an unpredictable way on the crystal growth conditions. Usually, diffusion and slow cooling techniques gave only the insulating phase, while simple slow evaporation of solvent at room temperature gave both phases.

The stoichiometries of these TCNQ complexes are given in Table II and were determined by elemental analysis and in case of **6b** by electron microprobe analysis for sulfur.[49]

References and Notes

(1) (a) IBM Thomas J. Watson Research Center; (b) IBM Research Laboratory.
(2) (a) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973). (b) Review of TTF modifications: M. Narita and C. U. Pittman, Jr., *Synthesis*, 489 (1976).
(3) Some recent TCNQ modifications: R. C. Wheland and E. L. Martin, *J. Org. Chem.*, **40**, 3101 (1975); see also B. P. Bespalov and V. V. Titov, *Russ. Chem. Rev. (Engl. Transl.)*, **44**, 1091 (1975); R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976); R. C. Wheland, *ibid.*, **98**, 3926 (1976); C. S. Jacobsen, J. R. Andersen, K. Bechgaard, and C. Berg, *Solid State Commun.*, **19**, 1209 (1976); A. J. Schultz, G. D. Stucky, R. A. Craven, M. J. Schaffman, and M. B. Salamon, *ibid.*, **98**, 5191 (1976); J. R. Andersen, R. A. Craven, J. E. Weidenborner, and E. M. Engler, *J. Chem. Soc., Chem. Commun.*, 526 (1977).
(4) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974).
(5) E. M. Engler and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, 671 (1975).
(6) Alternate syntheses of TSeF and DSeDTF have appeared: M. V. Lakshmikanthan and M. P. Cava, *J. Org. Chem.*, **41**, 882 (1976); M. V. Lakshmikanthan, M. P. Cava, and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 383 (1975).
(7) A. N. Block, J. P. Ferraris, D. O. Cowan, and T. O. Poehler, *Solid State Commun.*, **13**, 753 (1973).
(8) J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, *Tetrahedron Lett.*, 2553 (1973).
(9) R. L. Greene, J. J. Mayerle, R. Schumaker, G. Castro, P. M. Chaikin, S. Etemad, and S. J. LaPlaca, *Solid State Commun.*, **20**, 943 (1976).
(10) E. M. Engler and V. V. Patel, *Tetrahedron Lett.*, 423 (1976).
(11) H. K. Spencer, M. V. Lakshmikanthan, M. P. Cava, and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 867 (1975).
(12) K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J. Chem. Soc., Chem. Commun.*, 937 (1974).
(13) A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Lett.*, **34**, 1561 (1975).
(14) C. Berg, K. Bechgaard, J. R. Andersen, and C. S. Jacobsen, *Tetrahedron Lett.*, 1719 (1976).
(15) Reviews: (a) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974); (b) A. N. Bloch, D. O. Cowan, and T. O. Poehler in "Energy and Charge Transfer in Organic Semiconductors", K. Masuda and M. Silver, Ed., Plenum Press, New York, N.Y., 1974; (c) A. J. Heeger and A. F. Garito in "Low Dimensional Cooperative Phenomena", H. J. Keller, Ed., Plenum Press, New York, N.Y., 1975, (d) A. J. Berlinsky, *Contemp. Phys.*, **17**, 331 (1976); (e) E. M. Engler, *Chemtech*, **6**, 274 (1976); (f) J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.*, **16**, 519 (1977).
(16) Recently, a bipyridinium TCNQ salt was reported to be metallic to <1 K. See G. J. Ashwell, D. D. Eley, and M. R. Willis, *Nature (London)* **259**, 201 (1976); G. J. Ashwell, D. D. Eley, M. R. Willis, and J. Woodward, *Phys. Status Solidi B*, **79**, 629 (1977). However, these results have been disputed: R. B. Somorno, V. Hadek, S. P. S. Yen, A. Rembaum, C. Hsu, R. J. Deck, T. Datta, and A. M. Hermann, *ibid.*, **81**, 281 (1977).
(17) (a) E. M. Engler, B. A. Scott, S. Etemad, T. Penney, and V. V. Patel, *J. Am. Chem. Soc.*, **99**, 5909 (1977); (b) S. Etemad, E. M. Engler, T. Penney, B. A. Scott, and T. D. Schultz, *Phys. Rev. Sect. B*, **17**, 513 (1978).
(18) Y. Tomkiewicz, E. M. Engler, and T. D. Schultz, *Phys. Rev. Lett.*, **35**, 456 (1975).
(19) T. E. Phillips, T. J. Kristenmacher, A. N. Bloch, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 334 (1976).
(20) J. R. Cooper, M. Weger, D. Jerome, D. Lefur, K. Bechgaard, A. N. Bloch, and D. O. Cowan, *Solid State Commun.*, **19**, 749 (1976).
(21) R. H. Friend, D. Jerome, J. M. Fabre, L. Giral, and K. Bechgaard, *J. Phys.*, to be published.

(22) Reference 14 describes a modification of HMTSeF in which sulfur replaces the β-methylene (i.e., β-DTTSeF).

(23) Other syntheses of HMTTF: (a) E. Fanghänel, L. van Hink, and G. Schukat, *Z. Chem.*, **16**, 317, 360 (1976); (b) H. K. Spencer, M. P. Cava, F. G. Yamagishi, and A. F. Garito, *J. Org. Chem.*, **41**, 730 (1976); P. Delhaes, S. Flandrois, J. Amiell, G. Keryer, E. Toreilles, J. M. Fabre, L. Giral, C. S. Jacobsen, and K. Bechgaard, *J. Phys.*, 233 (1977).

(24) For earlier references on this cyclization see E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1708 (1964); I. D. Rae, *Int. J. Sulfur Chem.*, **1**, 59 (1971); A. K. Bhattacharya and A. G. Hortmann, *J. Org. Chem.*, **39**, 95 (1974), and references cited therein; R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, **99**, 5521 (1977).

(25) (a) F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1435 (1970); (b) D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971); (c) S. Hünig, G. Kiesslich, H. Quast, and D. Scheutzow, *Justus Liebigs Ann. Chem.*, 310 (1973).

(26) E. Klingsberg, *J. Am. Chem. Soc.*, **86**, 5290 (1964).

(27) For the naming of the heterofulvalenes presented in this paper, the 1,4,5,8-tetraheterofulvalene system is chosen as the parent ring.

(28) A convenient, high-yield synthesis of 1,2,3-selenadiazoles has been discovered by I. Lalezari, A. Shafiee, and M. Yalpani, *Tetrahedron Lett.*, 5105 (1969); I. Lalezari, A. Shafiee, and M. Yalpani, *J. Org. Chem.*, **36**, 2836 (1971).

(29) Phosphorus base coupling is currently the only effective means of coupling the selenium analogues of TTF. See ref 17a for discussion. See also ref 11.

(30) E. M. Engler, R. R. Schumaker, and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, 835 (1977).

(31) E. M. Engler and V. V. Patel, *Tetrahedron Lett.*, 423 (1976).

(32) ¹H NMR was able to show the presence of cis and trans isomers in DSeDTF (ref 5) and in DMDSeDTF (ref 10).

(33) The crystal structure of β-MeHMTSeF has recently been determined by S. J. LaPlaca, IBM Research (unpublished work). It confirms the presence of the methyl groups in the β positions. In the samples investigated, crystallization apparently has lead to preferential enrichment in the syn isomer.

(34) For earlier references on this cyclization see (a) A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.*, **17**, 1924, 1931 (1969); (b) ref. 8.

(35) For an analogous cyclization involving replacement of oxygen by sulfur see P. Rioult and J. Vialle, *Bull. Soc. Chim. Fr.*, 4478 (1968).

(36) For earlier references on this cyclization see E. Campaigne and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1703 (1964); E. Fanghänel, *Z. Chem.*, **1**, 58 (1967).

(37) A. Roxenbaum, H. Kirchberg, and E. Leibnitz, *J. Prakt. Chem.*, **19**, 1 (1963).

(38) T. Amano, H. Kuroda, and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **41**, 83 (1968); J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).

(39) R. Foster "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969.

(40) H. K. Spencer, M. P. Cava, and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 966 (1976).

(41) F. G. Yamagishi, D. J. Sandman, A. F. Garito, and A. J. Heeger, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., March 1973, No. ORGN-12.

(42) R. P. Shibaeva and O. V. Yarochkina, *Sov. Phys. Dokl.*, **20**, 304 (1975).

(43) J. P. Ferraris and F. I. Mopsick, *Chem. Eng. News* (Sept 16, 1974); see also K. G. R. Sundelin, *ibid.* (Aug 5, 1974).

(44) For the preparation of less dangerous hexafluorophosphate salts see L. R. Melby, H. D. Hartzler, and W. A. Sheppard, *J. Org. Chem.*, **39**, 2456 (1974).

(45) L. Henriksen and E. S. S. Kristiansen, *Inst. J. Sulfur Chem.*, Part A, **2**, 133 (1972).

(46) C. C. Price and J. M. Jusge, *Org. Synth.*, **45**, 22 (1965).

(47) For an overview of some of these techniques see J. R. Andersen, E. M. Engler, and K. Bechgaard in the Proceedings of the New York Academy of Sciences "Conference on Synthesis and Properties of Low Dimensional Materials", New York, N.Y., June 13–16, 1977, to be published.

(48) For information on this technique see L. B. Coleman, *Rev. Sci. Instrum.*, **46**, 1125 (1975).

(49) For a description of this method as applied to the analysis of organic charge transfer complexes see ref 17a.

Oxygen-17 Magnetic Resonance Study of Oxygen Exchange between Arsenite Ion and Solvent Water

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Abstract: Oxygen-17 magnetic resonance spectra of aqueous solutions of sodium arsenite were measured for $0.6 < [As(III)] < 4.1\ m$, $10 < t < 90$ °C. Line broadening of the water resonance in the 40–90 °C range gives the rate of oxygen exchange between $AsO(OH)_2^-$ and solvent water. Exchange takes place via a first-order pathway, $\Delta S_1^{\ddagger} = -120 \pm 3$ J K^{-1} mol^{-1}, $\Delta H_1^{\ddagger} = 25 \pm 1$ kJ mol^{-1}, and a pathway second-order in arsenite, $\Delta S_2^{\ddagger} = -102 \pm J$ K^{-1} mol^{-1}, $\Delta H_2^{\ddagger} = 33 \pm 4$ kJ mol^{-1}. Rates were measured using solutions of pH ~10.2; exchange appears to be only slightly faster in solutions of lower pH.

Introduction

Despite the use of arsenic(III) oxide, As_4O_6, by generations of analysts as a redox standard, remarkably little is known of the aqueous chemistry of As(III). Indeed, less than a decade has passed since the structures of arsenous acid and arsenite ion in aqueous media were finally established by Raman spectroscopy: trigonal pyramidal $As(OH)_3$ and $AsO(OH)_2^-$.[1,2]

An attempt was made in 1940 to measure the rate of oxygen exchange between arsenite ion and solvent water, but the exchange proved too fast for the isotopic exchange technique used.[3] Apparently because nucleophilic displacements on arsenite are very rapid, only two kinetic studies of As(III) substitution reactions have come to our attention and both involve As(III) as a catalyst: $AsO(OH)_2^-$ catalyzes the hydration of carbon dioxide,[4] and $As(OH)_3$ (and perhaps $AsO(OH)_2^-$) catalyzes the exchange of oxygen between dihydrogen arsenate, $AsO_2(OH)_2^-$, and water.[5] As the first of a series of studies of equilibria and kinetics of reactions involving As(III), we report here the measurement of the rate of oxygen exchange

between arsenite ion and solvent water by ¹⁷O magnetic resonance line broadening.

Experimental Section

Reagent grade sodium arsenite (Baker and Adamson) was used without purification for preparation of As(III) solutions. Analysis of this material showed that 23.6 mol % of the As(III) was present as As_4O_6, the remainder as $NaAsO_2$.

Solutions for ¹⁷O NMR spectra were prepared on a vacuum line. A weighed amount of dry sodium arsenite was placed in one section of a Y-shaped sample tube. An aliquot of sodium hydroxide or *p*-toluenesulfonic acid solution was pipetted into the other section of the sample tube and the water pumped off. About 2 g of ¹⁷O-enriched water (ca. 5% enrichment) was then distilled under vacuum into the sample tube. The ¹⁷O water reservoir was weighed before and after the distillation so that the molal concentration of As(III) could be computed. The enriched water was recovered after running the spectra and used for subsequent samples.

¹⁷O NMR spectra were recorded at 7.5 MHz (13 kG) on a Varian wide-line NMR spectrometer equipped with a 12-in. magnet and flux stabilizer. To ensure rf stability, the Varian V-4210A variable frequency unit was locked to an external frequency synthesizer (Syntest