Synthesis of *sym*-(*E*/*Z*)-Diselenadithiafulvalene

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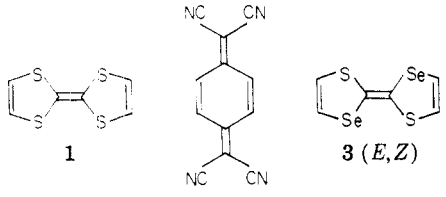
sym-Diselenadithiafulvalene (**3**) has been synthesized as an inseparable *E,Z* isomer mixture by two fundamentally different routes. The first synthesis proceeds via ethylene diselenocyanate (**9**), ethane-1,2-diselenol (**8**), 1,3-diselenolane-2-thione (**7**), 4,5-bis(carbomethoxy)-1,3-thiaselenole-2-selone (**12**), and tetrakis(carbomethoxy)-*sym*-diselenadithiafulvalene (**13**). The second synthesis, which involves a greatly improved route to 1,3-thiaselenole-2-selone (**18**), provides the most practical method available for the preparation of larger quantities of **3**.

Tetrathiafulvalene (TTF, **1**) and its derivatives are compounds of much current interest in solid-state physics, in view of the unusually high electrical conductivity of the crystalline charge-transfer salts which most of them form with tetracyanoquinodimethane (TCNQ, **2**).[1] In the

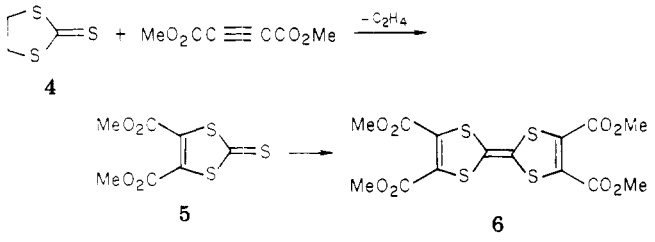


course of searching for charge-transfer salts having superior conductivity properties, considerable effort has been expended on the synthesis of tetrathiafulvalene analogues in which some or all of the sulfur atoms have been replaced by the more polarizable chalcogen selenium.[2a-c]

In 1975, we first disclosed a synthesis of *sym*-diselenadithiafulvalene (DSeDTF, **3**).[3] We now report full details of this work, as well as details of a second and more practical synthesis of **3**.

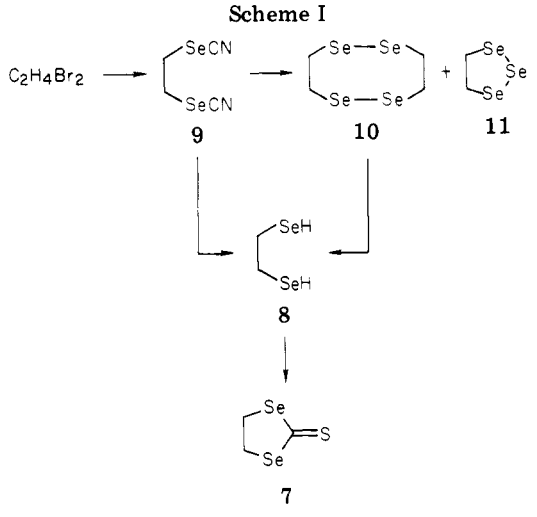
Results and Discussion

Selenocyanate Route to DSeDTF. One of the simplest and most efficient routes to a tetrathiafulvalene derivative involves the 1,3-dipolar addition of ethylene trithiocarbonate (**4**) to dimethyl acetylenedicarboxylate (DMAD) to give 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione (**5**),[4] followed by the trialkyl phosphite coupling of the latter to give tetrakis(carbomethoxy)tetrathiafulvalene (**6**).[5]



The formation of **5** from **4** by a concerted addition of DMAD to **4** requires that the thione sulfur of **5** be derived from a dithiolane sulfur of **4** and that a dithiole sulfur of **5** be derived from the thione sulfur of **4**; mechanistic studies on closely related systems support this hypothesis. It follows, therefore, that the previously unreported 1,3-diselenolane-2-thione (**7**) should be the most suitable and unambiguous dipolarophile for the synthesis of a 1,3-thiaselenole intermediate.

Scheme I



The obvious precursor of thione **7**, ethane-1,2-diselenol (**8**), has not been described in the literature. The closely related ethylene diselenocyanate (**9**), however, has been known since 1890 and was obtained by the action of alcoholic potassium selenocyanate on ethylene dibromide.[6] We have found that **9** can be easily and inexpensively made in quantity by preparing potassium selenocyanate in situ in dimethyl sulfoxide and reacting the resulting solution directly with ethylene dibromide. As reported by Hagelberg, selenocyanate **9** reacts readily with alcoholic alkali to give, in high yield, a very sparingly soluble yellow compound assigned the structure of 1,2,5,6-tetraselenocane (**10**).[6] We have now confirmed this tetraselenocane structure by mass spectrometry: the mass spectrum of **10** is unusual in showing the progressive loss of two ethylene units, leaving behind a strong Se_4 cluster ion. Unpurified tetraselenocane is contaminated with a much more soluble, odoriferous yellow compound, mp 160 °C dec, after sublimation at 100 °C. Spectroscopic analysis showed this compound to be 1,2,3-triselenacyclopentane (**11**), the parent substance of a new and unexpectedly isolable ring system. The mechanism of formation of **11** is not entirely clear, but it may arise from a side reaction involving fragmentation of selenocyanate **9** to selenide ion, followed by attack of the latter on additional selenocyanate.

(1) Garito, A. F.; Heeger, A. J. *Acc. Chem. Res.* **1974**, *7*, 232.
(2) (a) Engler, E. M.; Patel, V. V. *J. Am. Chem. Soc.* **1974**, *96*, 7376. (b) Spencer, H. K.; Lakshmikantham, M. V.; Cava, M. P.; Garito, A. F. *J. Chem. Soc., Chem. Commun.* **1975**, 867. (c) Bechgaard, K.; Cowan, D. O.; Bloch, A. N. *Ibid.* **1974**, 937.
(3) Lakshmikantham, M. V.; Cava, M. P.; Garito, A. F. *J. Chem. Soc., Chem. Commun.* **1975**, 383.
(4) Easton, D. B. J.; Leaver, D. *Chem. Commun.* **1965**, 585.
(5) Pittman, C. U., Jr.; Narita, M.; Liang, Y. F. *J. Org. Chem.* **1976**, *41*, 2855.
(6) Hagelberg, L., *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 1092.

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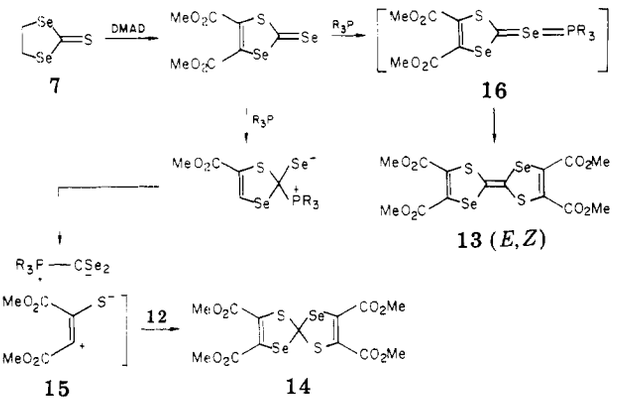
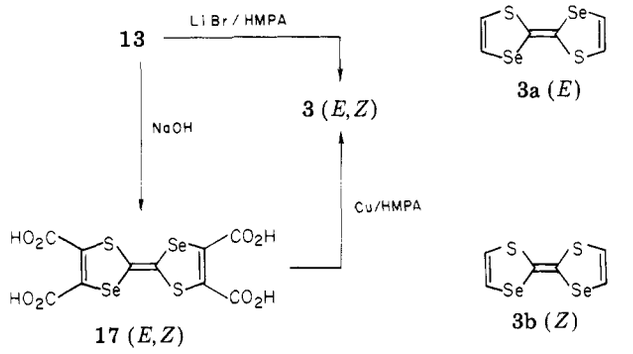
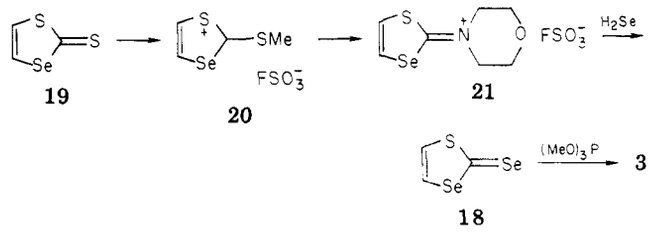
Scheme II



Scheme III



Scheme IV



Attempts to effect a reductive cleavage of tetraselenocane **10** to diselenol **8** with sodium borohydride were unsuccessful (Scheme I). Overreduction to selenide ion took place, as evidenced by the copious precipitation of red selenium when the solution was exposed to air. On the other hand, at least partial cleavage of tetraselenocane **10** to the dianion of diselenol **8** was achieved by the action of sodium in liquid ammonia, since subsequent treatment with thiophosgene afforded the desired thione **7** as orange needles, mp 74 °C, albeit only in 15% yield. Better results were obtained when diselenocyanate **9** was reduced by hypophosphorous acid under carefully defined conditions, as described in the Experimental Section. The resulting diselenol **8** formed a heavy colorless oil with an odor reminiscent of ethane-1,2-dithiol; on exposure to air it was rapidly oxidized to the tetraselenocane **10**. Without further characterization, the diselenol was reacted with (thiocarbonyl)diimidazole, to give thione **7** in 33% overall yield from diselenocyanate **9**.

Thione **7** reacted readily with DMAD in refluxing toluene to give 4,5-bis(carbomethoxy)-1,3-thiaselenole-2-selone (**12**) as bright red needles: mp 105 °C; 90% yield (Scheme II). Selone **12** was coupled by heating with triphenylphosphine in benzene to give the red-brown tetraester **13** (mp 138 °C), in 50% yield; ester **13**, while behaving as a single pure compound, is assumed to be a random mixture of *E* and *Z* isomers. A yellow crystalline compound (mp 100 °C) was also isolated in 14% yield from the coupling reaction. On the basis of its spectroscopic properties, it was assigned the spiran structure **14**. A possible mechanism for the formation of spiran **14** involves *nucleophilic* attack of the phosphine at the selone carbon of **12**, loss of a phosphine–carbon diselenide adduct, and addition of the resulting 1,3-dipole **15** to a second molecule of **12**, as shown in Scheme II. Normal selone coupling, in contrast, probably involves initial *selenophilic* attack of phosphine on the selone function with the formation of the primary intermediate **16**.

Removal of the ester groups from tetraester **13** was at first carried out in two steps. Alkaline hydrolysis of **13** afforded, after acidification, an almost quantitative yield of the black tetracarboxylic acid **17** (Scheme III). Copper-catalyzed decarboxylation of **17** in hot hexamethylphosphoramide (HMPA) gave the desired DSeDTF (**3**) in 34% yield. It was found later that tetraester **13** could be directly decarbomethoxylated on heating with lithium bromide in HMPA, giving **3** in 59% yield in one operation.

sym-Diselenadithiafulvalene (DSeDTF, **3**) crystallized from hexane as orange-red prisms which, after gradient sublimation, melted at 118.7–118.9 °C. Rapid chilling of a hexane solution of **3** caused the separation of a yellow crystalline polymorph which, on contact with the solvent at room temperature, reverted to the orange-red form. Its ultraviolet–visible spectrum is recorded in the Experimental Section.

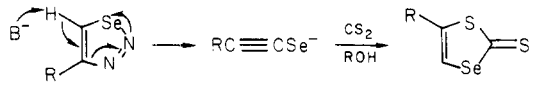
In agreement with the observations of Engler and Patel,[7] the 220-MHz NMR spectrum of **3** shows it to consist of a mixture of geometrical isomers (**3a** and **3b**). Although these isomers could not be separated by TLC or high-pressure LC, they appear to be quite stable thermally, since their NMR signals do not coalesce on heating to 90 °C. The two isomers are present in a ratio of 57:43. A recent X-ray crystallographic study of **3** has failed to identify individual units of **3a** and **3b**, and it appears most likely that the *E* and *Z* isomers are randomly distributed in the crystal lattice.[8]

Selenadiazole Route to DSeDTF. A second synthesis of DSeDTF was reported by Engler and Patel very soon after the appearance of our preliminary paper.[7] This second synthesis, which consists of only two steps, involves the reaction of sodium acetylide with sulfur, followed by carbon diselenide and then a proton source to give 1,3-thiaselenole-2-selone (**18**); trimethyl phosphite coupling of **18** affords DSeDTF (**3**). The disadvantage of this synthesis is that, although the phosphite coupling step proceeds in good yield (up to 80%), the required selone **18** was obtained in only 0.82% yield from the toxic and costly CSe_2 after a chromatographic separation from five other closely related thiones and selones formed as byproducts from an unexpected sulfur–selenium scrambling process.[9] 1,3-Thiaselenole-2-thione (**19**), available from sodium acetylide, selenium, and carbon disulfide in just over 5% yield after a similar five-component chromatographic separation,[9] could not be coupled to give DSeDTF.[7]

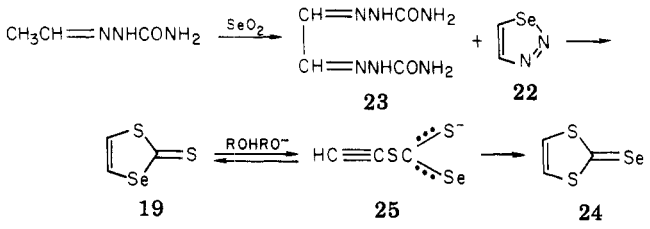
Some time ago, we reported a convenient procedure for the conversion of annelated derivatives of thione **19** to the corresponding selones.[2b] We have now found this procedure to be quite satisfactory in the case of the parent compound. Thus, thione **19** reacts readily with methyl fluorosulfonate to give the highly crystalline *S*-methyl fluorosulfonate **20** (Scheme IV). Reaction of **20** with

(7) Engler, E. M.; Patel, V. V. *J. Chem. Soc., Chem. Commun.* **1975**, 671.
(8) Belsky, V. K.; Voet, D. *J. Cryst. Mol. Struct.* **1978**, *8*, 9.
(9) Engler, E. M.; Patel, V. V. *J. Org. Chem.* **1975**, *40*, 387.

Scheme V



Scheme VI



morpholine affords the white crystalline morpholinium salt **21**, which is converted to selone **18** by hydrogen selenide: the overall yield of **18** from **19** is 50%. We therefore focused our efforts upon a simplified route to thione **19**.

The synthesis and base-catalyzed decomposition of various 1,2,3-selenadiazoles has been studied extensively by a group of Iranian chemists in recent years.[10] Among other observations, it has been found that base-catalyzed fragmentation of a series of 4-aryl-1,2,3-selenadiazoles, followed by carbon disulfide treatment of the intermediate selenolate salts, afforded the corresponding thiaselenole-2-thiones in excellent yields[11] (Scheme V). The behavior of the unsubstituted selenadiazole in this reaction was not reported.

The parent 1,2,3-selenadiazole (**22**) is available by the reaction of acetaldehyde semicarbazone with selenium dioxide[10] (Scheme VI). In an improved procedure using a two-phase system with a phase-transfer catalyst, **22** is easily obtained in quantity in 30–40% yield from acetaldehyde semicarbazone; glyoxal semicarbazone (**23**) is formed as a byproduct.

The reaction of selenadiazole with potassium *tert*-butoxide in *tert*-butyl alcohol, followed by addition of carbon disulfide, gave a low-yield mixture of the desired yellow thione **19** and the isomeric red selone **24**. Under the same reaction conditions, selone **24** was not converted to thione **19**, but thione **19** was converted in high yield to selone **24**. Since the rearrangement of **19** to **24** must proceed via the ambident anion **25**, this result suggests either that selone **24** is thermodynamically favored over thione **19** or that selone **24** is less acidic than thione **19** and, once formed, is not reequilibrated with anion **25**.

Fortunately, conditions were found for the formation of **19** without concomitant isomerization. Thus, addition of solid potassium *tert*-butoxide to a solution of selenadiazole in *tert*-butyl alcohol–dimethyl formamide containing a large excess of carbon disulfide afforded the pure thione **19** in 55% yield after sublimation.

Thus, DSeDTF (**3**) may now be obtained in remarkably high yield (up to 24%) from the readily prepared 1,2,3-selenadiazole (**22**), making this interesting π donor much more accessible for physicochemical studies.

Experimental Section

Melting points were determined by using a micro hot stage and are uncorrected. NMR ($CDCl_3$ containing tetramethyl silane as internal standard unless otherwise stated), low resolution mass, and ultraviolet–visible spectra (cyclohexane solutions) were determined by using JEOL-100 and Perkin-Elmer 270B and 202 spectrometers, respectively. All selenium-containing mass peaks are reported for ^{80}Se. Undue skin contact with the selenium-containing compounds was avoided, and all the reactions were carried out in a well-ventilated hood. Addition of laundry bleach removed all traces of selenium stains from contaminated glassware, clothing, etc.

Ethylene Diselenocyanate (9). To a stirred solution of potassium cyanide (25 g) in dry dimethyl sulfoxide (100 mL), protected from moisture, was added selenium (32 g) portionwise at 120–130 °C, with a waiting period for dissolution of each lot before the next addition. After the addition was over, the mixture was stirred for 1 h more at 140 °C, cooled to room temperature, and treated with ethylene dibromide (25 mL). After being stirred at 50 °C for 2 h, the mixture was diluted with water. The precipitated solid was filtered, washed, dried, and recrystallized from ethanol–chloroform to yield pure ethylene selenocyanate: 34 g (77% yield); mp 136 °C after sublimation at 125 °C (lit.[6] mp 138 °C).

1,2,5,6-Tetraselenocane (10) and 1,2,3-Triselenacyclopentane (11). Ethylene diselenocyanate (7 g) was added in portions to a vigorously stirred, ice-cooled solution of potassium hydroxide (4 g) in methanol (25 cm^3). After the addition was over (~0.5 h), the yellow suspension was stirred 15 min more, diluted with water, and filtered. The foregoing crude yellow compound (4 g) was extracted in a Soxhlet cup with chloroform for 2 days. Concentration of the filtered chloroform extract furnished the triselenide **11** as a yellow crystalline solid (500 mg), decomposing with gas evolution at 160–170 °C after subliming at 100 °C; mass spectrum, *m/e* (relative intensity) 268 (M^+, 55). Anal. Calcd for $C_2H_4Se_3$: *m/e* 265.7820. Found: *m/e* 265.7823.

The chloroform-insoluble yellow powder in the Soxhlet cup was recrystallized from ethylene dibromide (25 cm^3) to furnish the tetraselenide **10** as a microcrystalline material: mp 128 °C (lit.[6] mp 130.5 °C); 2.8 g; mass spectrum, *m/e* (relative intensity) 376 (M^+, 20), 348 (9), 320 (20), 268 (80), 240 (63), 188 (37), 160 (90), 108 (100), 80 (50); NMR (Me_2SO-d_6) δ 3.45 (s).

1,3-Diselenolane-2-thione (7). (a) From 1,2,5,6-Tetraselenocane (10). To a stirred suspension of tetraselenide **10** (108 mg) in liquid ammonia (100 cm^3) was added sodium (30 mg). After 15 min, the blue color was gone, leaving a clear solution in place of the original yellow suspension. Addition of more sodium (~10 mg) led to a blue color. After 0.5 h, methanol was added dropwise to discharge the blue color. The resulting creamy white residue, after evaporation of all the ammonia under nitrogen, was dissolved in acetonitrile (10 cm^3) and treated with thiophosgene (0.04 cm^3; **caution**, toxic!) in acetonitrile (2 cm^3). After the mixture was stirred for 1 h, the solvent was removed, and the residue was extracted into chloroform. The residue from the chloroform extract was chromatographed on silica by using chloroform as eluant to yield a red oil which crystallized from hexane to give the highly crystalline thione **7**: mp 74 °C; 10 mg (15%); [the chloroform-insoluble portion, after being washed with water to free inorganic salts, was mainly recovered starting material (64 mg)]; mass spectrum, *m/e* (relative, intensity) 232 (M^+, 100), 204 (15), 160 (47), 124 (79), 108 (95); NMR δ 4.26 (s); UV λ_{max} 210 nm, 220 (log ϵ 3.82), 270, 290 (3.22), 330 (4.10). Anal. Calcd for $C_3H_4SSe_2$: *m/e* 231.8363. Found: *m/e* 231.8341.

(b) From Ethylene Selenocyanate (9). Well-powdered ethylene diselenocyanate (**9**, 2.4 g) and hypophosphorous acid (50%; 60 mL) was placed in a three-necked flask fitted with a CO_2 inlet, a thermometer, and a condenser. The condenser was connected in series to two traps cooled in ice and dry ice/acetone, respectively. The mixture was stirred magnetically and heated at 80–90 °C with a gentle stream of CO_2 sweeping through. Ethanediselenol which formed was swept out of the flask and condensed in the traps. When most of the solid in the reaction flask was reduced, the traps were disconnected, and the contents were extracted into ether under carbon dioxide. (The selenol is a heavy colorless malodorous liquid, stable under inert atmosphere but supersensitive to air.) The washed, dried ethereal extract containing ethanediselenol was treated with a freshly prepared solution of (thiocarbonyl)diimidazole (1 g) in benzene (10 mL). The deep orange mixture was filtered free of an insoluble material and washed with dilute hydrochloric acid followed by water. Evaporation of the orange ether–benzene solution, followed by crystallization from cyclohexane, furnished 1,3-diselenolane-2-thione (**7**, 0.773 g) as orange needles (yield 33%, mp 74 °C), identical in all respects with the foregoing sample.

(10) (a) Lalezari, I.; Shafiee, A.; Yalpani, M. *J. Org. Chem.* **1971**, *36*, 2836. (b) Lalezari, I.; Shafiee, A.; Yalpani, M. *Ibid.* **1973**, *38*, 338.
(11) Shafiee, A.; Lalezari, I.; Savabi, F. *Synthesis* **1977**, 764.

4,5-Bis(carbomethoxy)-1,3-thiaselenole-2-selone (12). A mixture of 1,3-diselenolane-2-thione (**7**, 1 g) and dimethyl acetylenedicarboxylate (0.6 mL) in toluene (25 mL) was refluxed for 1.5 h. After removal of toluene in vacuo, the residue was crystallized from methanol to yield the thiaselenole-2-thione **12**: 1.35 g (90%); mp 105 °C; mass spectrum, *m/e* (relative intensity) 346 (M^+ 100); NMR δ 3.91 (s), 3.89 (s); UV λ_{max} 215 nm (log ϵ 4.18), 310–315 (3.25), 400 (4.09), 540 (1.32). Anal. Calcd for $C_7H_6O_4SSe_2$: *m/e* 345.8316. Found: *m/e* 345.8310.

Tetrakis(carbomethoxy)-*sym*-(*E*/*Z*)-diselenadithiafulvalene (13) and Byproduct 14. A mixture of diester **12** (475 mg) and triphenylphosphine (400 mg) in benzene (30 mL) was refluxed for 2 h. The dark red solution was evaporated to dryness. Dry column chromatography of the residue on silica afforded tetraester **13** (261 mg) which was crystallized from methanol to yield red-orange crystals: mp 138 °C; 183 mg (50%); mass spectrum, *m/e* (relative intensity) 532 (M^+, 100); NMR δ 3.86 (s), 3.82 (s); UV λ_{max} 250 nm (log ϵ 4.39), 290 (4.43), 325 (4.03), 434 (3.44). Anal. Calcd for $C_{14}H_{12}O_8S_2Se_2$: *m/e* 531.8301. Found: *m/e* 531.8275.

The methanol mother liquor of crystallization of **13** upon being allowed to stand deposited a yellow highly crystalline material (50 mg, 14%). Recrystallization from a minimum of methanol furnished pure tetraester **14**: mp 100 °C; mass spectrum, *m/e* (relative intensity) 520 (M^+, 100); NMR δ 3.82 (s), 3.79 (s); UV λ_{max} 283 nm (log ϵ 4.11), 360 (3.86). Anal. Calcd for $C_{13}H_{12}S_2Se_2$: *m/e* 519.8305. Found: *m/e* 519.8295.

Tetracarboxy-*sym*-diselenadithiafulvalene 17. A mixture of tetraester **13** (0.18 g), aqueous sodium hydroxide (5 mL of 10% solution), and methanol (5 mL) was refluxed for 1.5 h. The resulting orange-red solution was acidified while still warm. The precipitated violet-black tetraacid **17** (0.149 g, mp >300 °C) was dried and used without further purification.

***sym*-(*E*/*Z*)-Diselenadithiafulvalene (3). (a) By Decarboxylation of the Tetraacid.** The dry acid (0.15 g) was suspended in hexamethylphosphoramide (2 mL), a trace of copper bronze was added, and the mixture was heated. At 130–140 °C, the color lightened considerably, and gas evolution was noticeable. After the mixture was maintained at 150–160 °C for ~20 min, it was cooled, poured into water, and extracted with ether–cyclohexane. Evaporation furnished DSeDTF (**3**): 50 mg (52%); mp 110 °C. Chromatography (SiO_2, benzene–cyclohexane) followed by recrystallization from hexane furnished material: mp 115 °C; 32 mg (33.8%). After gradient sublimation it had a melting point of 118.7–118.9 °C: mass spectrum, *m/e* (relative intensity) 300 (M^+ 100); NMR δ 6.82 (d, J = 6.5 Hz), 6.60 (J = 6.5 Hz) (57%), 6.71 (d, J = 6.5 Hz), 6.50 (J = 6.5 Hz) (43%) (this was unchanged up to 90 °C); UV (hexane) λ_{max} 210 nm (log ϵ 3.95), 235 (sh, 3.57), 282 (3.96), 297 (3.99), 325 (3.77), (sh, 2.99), 470 (2.30). Anal. Calcd for $C_6H_4S_2Se_2$: *m/e* 299.8050. Found: *m/e* 299.8086.

(b) Decarbomethoxylation of Tetraester 13. To a solution of the tetraester **13** (0.457 g) in hexamethylphosphoramide (15 mL) in a flat-bottomed flask was added LiBr (1.00 g), and the mixture was heated gradually on a hot plate. At 70–80 °C there was gas evolution (CH_3Br), and the solution lightened in color. The temperature was raised to 155 °C, and after 15 min at that temperature the dark mixture was cooled and diluted with aqueous sodium sulfate solution. Extraction with ether–cyclohexane and the usual workup furnished crude DSeDTF (0.217 g, 84%) which was recrystallized to give orange-red prisms of **3** (0.152 g, 59%; mp 116 °C), identical in all respects with the sample prepared by method a.

Improved Preparation of 1,2,3-Selenadiazole (22).[10] A well-stirred suspension of acetaldehyde semicarbazone (30 g) in methylene chloride (200 cm^3) in a wide-mouthed round-bottomed flask was treated with aqueous selenium dioxide (34 g, 200 cm^3) containing acetic acid (10 cm^3) and cetyltrimethylammonium bromide (~200 mg). Stirring was continued until nitrogen evolution virtually ceased (3 h). The insoluble red precipitate was filtered by suction and washed with hot methylene chloride. The pale yellow organic layer from the filtrate was separated, washed well with water, dried (Na_2SO_4), and evaporated to give the crude selenadiazole (15 g) as a pale yellow oil. Distillation yielded 14 g of colorless liquid (35%): bp 68–70 °C (40 mm); NMR δ 9.56 [d, 1 H, $J_{H,H}$ = 3 Hz, further split into a doublet of doublets by ^{77}Se (J_{SeH} = 40 Hz)], 8.31 (d, J = 3 Hz).[10] The red insoluble precipitate was boiled with a solution of potassium cyanide (6 g) in water (60 cm^3) to dissolve all the elemental selenium. The resulting yellowish white residue (5.92 g, mp >300 °C dec) was identical in all respects with glyoxal semicarbazone **23**. Acidification of the selenocyanate solution furnished red selenium (4 g).

1,3-Thiaselenole-2-thione (19). To a stirred mixture of selenadiazole **22** (8 g), carbon disulfide (50 cm^3), and *tert*-butyl alcohol (20 cm^3) in dimethyl formamide (50 cm^3) under argon at ice temperature was added potassium *tert*-butoxide (5.2 g) in portions, with a waiting period until nitrogen evolution slackened prior to each addition. Half an hour after the addition was over, the reaction mixture was diluted with ice-cold aqueous acetic acid. The dark carbon disulfide layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were washed, dried, and evaporated to yield the crude thione **19** as a tawny crystalline solid (6.7 g). Thione **19** was best purified by mixing with charcoal and subliming under reduced pressure (40–60 mm) in a fume hood at 100–110 °C to give bright yellow heavy needles: mp 60 °C (lit.[9] mp 60.5 °C); 6 g (55%).

Isomerization of Thione 19 to Selone 24. A solution of thione **19** (364 mg) and *tert*-butyl alcohol (0.5 cm^3) in DMF (2 cm^3) was treated with potassium *tert*-butoxide at room temperature. The resulting dark red mixture was diluted with aqueous acetic acid and was extracted with benzene–cyclohexane (1:2). Chromatography of the residue from this extract on silica with benzene–cyclohexane led to the isolation of starting material (70 mg in two crops, mp 58 °C) and a mixture of thione **19** and selone **24** (70 mg); elution with methylene chloride led to the recovery of the selone **24**: 200 mg; mp 59 °C (lit.[9] mp 59–60 °C). Prolonged exposure of thione **19** to alkali under the above conditions led to total conversion to selone.

Action of KO-*t*-Bu/*t*-BuOH in DMF on Selone 24. To a mixture of 50 mg of selone **24** in DMF (1 cm^3) and *t*-BuOH (0.5 cm^3) was added KO-*t*-Bu (20 mg). After 1 h, TLC indicated no thione, and workup led to recovery of the selone (30 mg).

1,3-Thiaselenole-2-morpholinium Fluorosulfonate (21). A solution of 1,3-thiaselenole-2-thione (**19**, 1.8 g) in 10 cm^3 of methylene chloride was treated slowly with methyl fluorosulfonate[12] (2 cm^3) at 0 °C with stirring. The salt oiled out and solidified to a crystalline mass upon rubbing with ether. The crude salt (3 g) was washed by decantation with anhydrous ether several times, redissolved in dry acetonitrile, and treated with dry morpholine (1 cm^3) at 0 °C. The mixture was stirred until all the methanethiol was eliminated. The reaction mixture was diluted with anhydrous ether to complete the precipitation of the morpholinium salt **21**. Filtration followed by recrystallization from acetonitrile–ether yielded white crystals: 2.7 g (79%); mp 190 °C dec. Anal. Calcd for $C_7H_{10}FNO_4S_2Se$: C, 25.15; H, 3.02; N, 4.19; S, 19.19. Found: C, 25.26; H, 3.16; N, 4.34; S, 19.30.

1,3-Thiaselenole-2-selone (18). The foregoing salt (**21**, 2 g) was suspended in 50% aqueous methanol (25 cm^3) containing 5 cm^3 of saturated sodium bicarbonate solution cooled in ice and under an argon atmosphere. Hydrogen selenide, liberated under an argon atmosphere by the dropwise addition of acifidied water on aluminium selenide (0.6 g), was passed through this salt solution and subsequently through lead acetate traps to destroy any unreacted excess hydrogen selenide. The reaction mixture, which turned yellow first, became orange-red. (Completion of the reaction was also indicated by the appearance of black lead selenide in the first trap.) Argon was blown through the system to drive off any excess unreacted hydrogen selenide before workup. The product was then extracted with methylene chloride, and the extract was washed with water and dried. Filtration followed by evaporation gave a red crystalline residue. Recrystallization from methylene chloride–hexane gave the selone **18**: 700 mg (52.6%); mp 80 °C (lit.[9] mp 80–81 °C).

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(12) Methyl fluorosulfonate is *extremely toxic*. Due precautions should be taken in the use of this reagent.

Registry No. 3a, 55681-24-8; **3b**, 55681-23-7; **7**, 56742-34-8; **9**, 4734-51-4; **10**, 3333-35-5; **11**, 73378-22-0; **12**, 56742-35-9; (*E*)-**13**, 73378-23-1; (*Z*)-**13**, 73378-24-2; **14**, 73378-25-3; (*E*)-**17**, 73378-26-4; (*Z*)-**17**, 73384-21-1; **18**, 53555-45-6; **19**, 1120-65-6; **21**, 73378-28-6; **22**, 26223-16-5; **23**, 31909-46-3; **24**, 53555-44-5; ethylene dibromide, 106-93-4; dimethyl acetylenedicarboxylate, 762-42-5; acetaldehyde semicarbazone, 591-86-6; morpholine, 110-91-8; potassium cyanide, 151-50-8; selenium, 7782-49-2.

Chiroptical Properties of Sulfenamides[1]

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The ORD (and in some cases CD) spectra are presented for 11 sulfenamides of the structure R'SN(SO_2Ar)CH(CH_3)R (R' = CCl_3, 4-chloro-2-methylphenyl, 2-nitrophenyl, 2,4-dinitrophenyl; R = phenyl, 1-naphthyl, benzyl; Ar = *p*-tolyl). A number of the spectra exhibit intense Cotton effects characteristic of inherently dissymmetric chromophores near 200 nm. The configuration at the asymmetric carbon atom seems to be related to the sign of the long-wavelength transition (near 350 nm) in the 2,4-dinitrobenzenesulfenamides. This is ascribed to an equilibrium asymmetric induction from the asymmetric center into the sulfenamide chiral axis whose configuration is reflected by the sign of this Cotton effect. It is suggested that examination of such derivatives may provide a useful method for determination of the absolute configuration of amines.

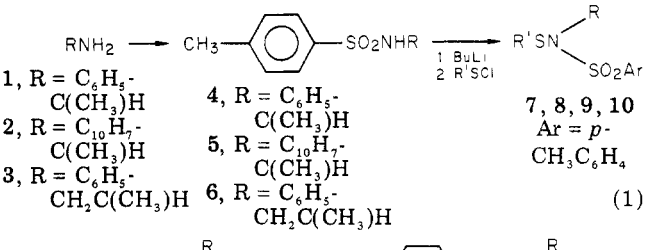
The chiroptical properties of compounds bearing sulfur-containing chromophores have been the subject of extensive experimental and theoretical work.[2] This work has been directed, for the most part, at functional groups with sulfur in the S^{II} and S^{IV} oxidation states. Among the S^{II} compounds, three classes are important, the sulfides, the disulfides, and the compounds with π bonding or π conjugation by divalent sulfur. The sulfenamides, however, represent a class of S^{II} compounds whose chirality is well established[3-5] but whose chiroptical properties have received almost no attention.[4]

Extensive NMR studies have demonstrated that the sulfenamide moiety can function as an axially chiral configurational unit. Thus, it was supposed that the sulfenamide moiety, if involved in an optically active transition, might give rise to Cotton effects of large magnitude since the same structural feature can function both as a chiral unit and as a chromophore (or part of a chromophore). In this regard the sulfenamide group is like the disulfide chromophore which has been described as an "inherently dissymmetric chromophore" rather than like the sulfide chromophore which is a symmetric chromophore which can suffer dissymmetric perturbation.[2a]

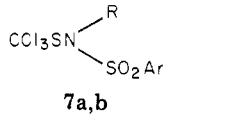
Ideally, examination of the chiroptical properties of the sulfenamide moiety would involve the optical activation of compounds containing the sulfenamide group as the sole chiral unit. However, the highest yet reported barrier for stereomutation at the sulfenamide chiral unit (21.4 kcal/mol)[3] is insufficient for optical stability at room temperature, and this is not yet possible. Nevertheless, it is possible to induce chirality into the sulfenamide chiral unit by equilibrium asymmetric induction.[5] We have chosen this approach and have prepared several *N*-arenesulfonylsulfenamides whose ORD and/or CD spectra offer some information about the chiroptical properties of the sulfenamide group.

Results and Discussion

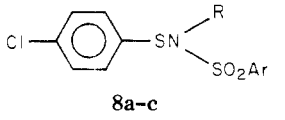
Three optically active amines of known absolute configuration, (+)-(*R*)-α-methylbenzylamine[6] (**1**), (+)-(*R*)-1-(α-naphthyl)ethylamine[7] (**2**), and (−)-(*R*)-1-methyl-2-phenylethylamine[8] (**3**), were converted via their sulfonamides into the 11 *N*-(arenesulfonyl)sulfenamides **7**, **8**, **9**, and **10** as indicated in eq 1. The spectral features (extrema and crossover points) of their ORD spectra are summarized in Table I.



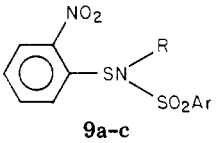
1, R = $C_6H_5C(CH_3)H$
2, R = $C_{10}H_7C(CH_3)H$
3, R = $C_6H_5CH_2C(CH_3)H$
4, R = $C_6H_5C(CH_3)H$
5, R = $C_{10}H_7C(CH_3)H$
6, R = $C_6H_5CH_2C(CH_3)H$
7, 8, 9, 10 Ar = *p*-$CH_3C_6H_4$ (1)



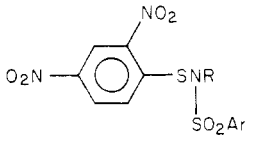
7a,b



8a-c



9a-c



10a-c

a, R = $C_6H_5C(CH_3)H$; **b**, R = $C_{10}H_7C(CH_3)H$; **c**, R = $C_6H_5CH_2C(CH_3)H$

(1) (a) Stereochemistry in Trivalent Nitrogen Compounds. 36. For the previous paper in this series see ref 3. (b) This work was supported by the National Science Foundation.
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