Heterofulvalenes. I. 5-Aza- and 6-Aza-1,4-dithiafulvalenes

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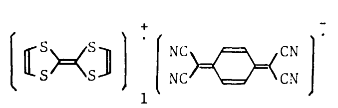
5-Aza, 2,3-benzo-5-aza-, 6-aza-, and 2,3-benzo-6-aza-1,4-dithiafulvalenes were synthesized and their spectroscopic properties are described. For example, the reaction of 2-methylthio-1,3-dithiolylium iodide with pyrrole gave 2-(2-pyrrolyl)-1,3-dithiolylium iodide in a 92% yield, which was treated with DBU, giving rise to 5-aza-1,4-dithiafulvalene as thermally-stable orange crystals in an 82% yield. Several reactions found during the course of these synthetic studies are also reported.

Recent findings concerning the highly-conductive charge-transfer salt (**1**) of tetrathiafulvalene and tetracyanoquinodimethane have created a wide and expanding interest in convenient methods of synthesizing a variety of tetrathiafulvalene derivatives and their tetraselenafulvalene analogs.1) The synthesis of azadithiafulvalenes, **2b** and **c**, and **3c** and **d**, has been reported by Gompper and Weiss.2) However, no report of the synthesis of the parent compounds, **2a** and **3a**, has appeared, although 1,4-dithiafulvalene (**4**) has already been synthesized.3) Compounds **2** and **3** are iso-π-electronic with **4** and sesquifulvalene (**5**)4) and may be aromatic if dipolar structures such as **2′** or **3′** contribute to the ground state of these molecules. Here, the synthesis of **2a**, **3b**, their benzo-derivatives, and their spectroscopic properties are reported. At the beginning of these studies, parent compounds **2a** and **3a** were considered too thermally unstable to be isolated because Gompper and Weiss were not able to isolate **2b** and **3c** (they can be maintained in acetonitrile at room temperature for several hours).2) The synthesis of benzo-derivatives of **2** and **3** were then undertaken in the expectation that they would be more stable than the parent compounds. The starting materials, **7**, **8**, and **9**, were easily obtained by reactions of benzodithiole **6** with pyrroles in acetic acid.5)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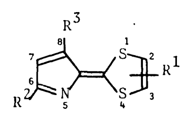
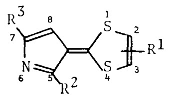
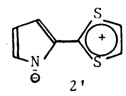
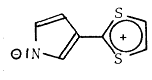


2a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Ph,\ R^2 = R^3 = Me$
c; $R^1 = R^2 = R^3 = Ph$



3a; $R^1 = R^2 = R^3 = H$
b; $R^1 = H,\ R^2 = R^3 = Me$
c; $R^1 = Ph,\ R^2 = R^3 = Me$
d; $R^1 = R^2 = R^3 = Ph$


2′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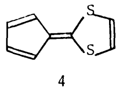
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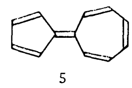
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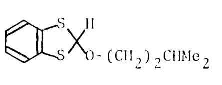
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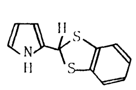
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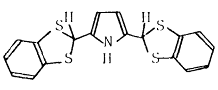
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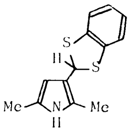
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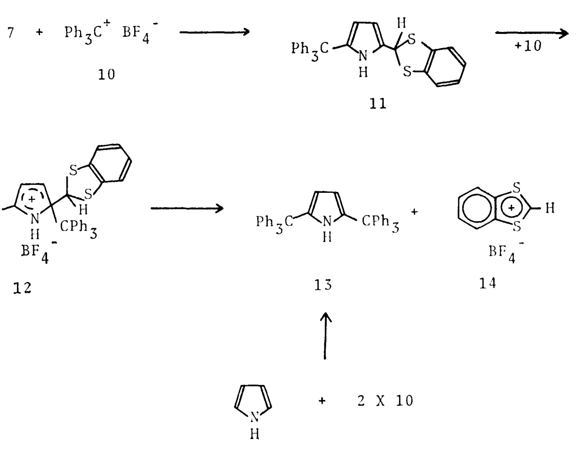
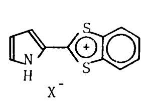
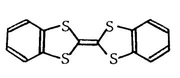
Trityl tetrafluoroborate (**10**) can abstract a hydride from 1,3-benzodithiole to give 1,3-benzodithiolylium tetrafluoroborate (**14**) in a good yield.6) Thus, the reaction of **7** with an equimolar amount of **10** was carried out in acetonitrile at room temperature with the expectation of obtaining the dithiolylium salt, **15a**. However, the reaction gave 2,5-tritylpyrrole (**13**) in a 54% yield (based on **10**). The use of 2 molar amounts of **10** gave **13** in a 62% yield. The structure of **13** was confirmed by comparison with an authentic sample prepared in a 71% yield by the reaction of 2 equivalents of **10** with pyrrole. The formation of **13** from **7** and **10** may proceed *via* the formation of **11** as a transient intermediate. This would not be unexpected in view of the facile formation of **13** by the action of 2 equivalents of **10** with pyrrole. Ipso-substitution to form a sterically-unfavorable intermediate, **12**, and subsequent elimination of the dithiolylium salt (**14**) produced **13** The formation of the heteroaromatic salt, **14**, serves as a driving force for the latter reaction. Actually, evidence of the formation of **14** is found in the fact that treatment of the reaction mixture with triethylamine gave dibenzotetrathiafulvalene (**16**) in a low yield (2%). The formation of **16** from **14** by treatment




15a; X = BF_4
b; X = ClO_4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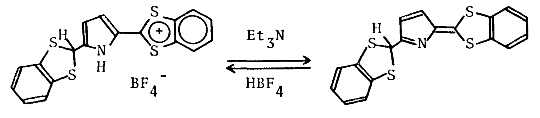
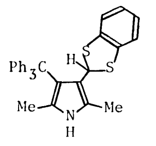
with a base is well documented.[6]

Although the reaction of **7** with **10** failed to give the expected product, treatment of **8** with **10** gave salt **17** as unstable yellowish-brown crystals in a 51% yield. Treatment of **17** with triethylamine in acetonitrile at room temperature quantitatively gave the azadithiafulvalene, **18**. Compound **18**, on being treated with tetrafluoroboric acid, gave salt **17**, but neither methyl iodide nor benzoyl chloride reacted with **18** in boiling acetonitrile or in acetonitrile at room temperature, respectively.



The reaction of **9** with **10** gave compound **19** (17%) and triphenylmethane (56%). Although the formation of triphenylmethane is indicative of the formation of the expected salt, **20a**, it was not isolated in pure form. Salt **14** also serves as hydride acceptor and is a milder reagent than **10**.[6,7] Therefore, **9** was allowed to react with **14**. The reaction carried out in acetonitrile at room temperature gave **20a** (20%), **21** (36%), and **22** (15%). Compound **14** in the reaction with **9** undergoes both hydride abstraction to form **20a** and electrophilic substitution to form **21**. The formation of compound **22** is the result of hydride abstraction from **21** by **14**. Salts **20a** and **22** could not be separated from each other, but the ratio of **20a** to **22** formed was easily determined by NMR analysis since both salts could be prepared by other methods described below. Compound **21** was prepared in a 93% yield from 2,5-dimethylpyrrole and 2 equivalents of **6** in acetic acid. Treatment of **21** with an equimolar amount of **14** gave salt **22** in a 76% yield. The reaction of **21** with **10** gave impure **22** in a diminished yield. Treating **22** with diazabicyclo[5.4.0]-undec-7-ene(DBU) gave the azathiafulvalene, **23**, in a 92% yield.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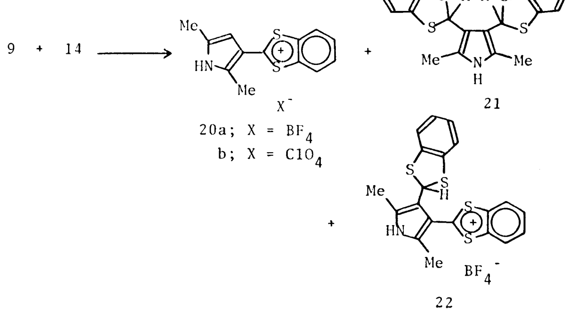
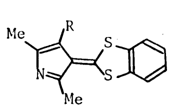
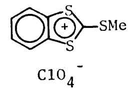



23; R = 1,3-Benzodithiol-2-yl
27; R = H

Since the reactions described above failed to produce clean samples of salts **15a** and **20a**, synthesis of these salts from salt **24**[8] was attempted. Pyrrole reacted smoothly with **24** in acetonitrile at room temperature and the expected perchlorate, **15b**, was obtained in an 84% yield. Similarly, salt **20b** was prepared from **24** and 2,5-dimethylpyrrole in a 67% yield. Treatment of an acetonitrile solution of **15b** with DBU gave the azadithiafulvalene, **25**, as an orange crystalline precipitate in a 31% yield. The addition of 2,3-dichloro-5,6-dicyano-*p*-benzo-quinone (DDQ) to the filtrate gave 1 : 1 charge transfer salt **26** of DDQ and **25** in a 37% yield. Salt **26** may consist of the radical anion of DDQ and the radical cation of **25** (the structure of **25** under active investigation in this laboratory). In a similar manner, salt **20b** was converted to **27** in a 68% yield.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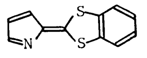
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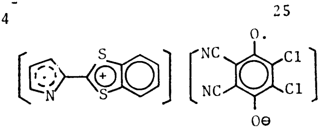
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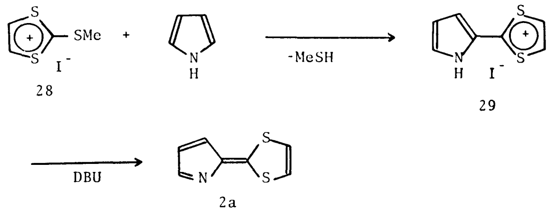
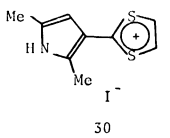
The finding that **25** and **27** thus obtained are thermally more stable than expected was encouragement to prepare parent compound **2a**. Thus, pyrrole was allowed to react with an equimolar amount of iodide **28**[9] in acetonitrile at room temperature for 2 days to gave the dithiolylium iodide, **29**, in a 92% yield. Treatment of **29** with DBU gave 5-aza-1,4-dithiafulvalene (**2a**) as orange crystals in an 82% yield. **2a** is thermally stable and can be stored in a refrigerator indefinitely. Similarly, salt **30** was prepared in an 83% yield from 2,5-dimethylpyrrole and **28**. Salt **30** was also converted to the thermally-stable azadithiafulvalene, **3b**, by treatment with DBU in

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a 70% yield. **3b** is less stable than **2a** and decomposed to tarry materials in solution.

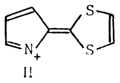
NMR data for 1,3-dithiolylium salts and azadithiafulvalenes are summarized in Table 1. For comparison with these compounds, data for **7**, **8**, and **9** were also included. In the NMR spectrum of **8**, the pyrrole-ring proton signal appears at δ 6.07 as a doublet (due to long-range coupling with the N–H proton[10)]).

On the other hand, the pyrrole-ring proton signal of the dithiolylium salt, **17**, occurs as two doublets at δ 6.78 and 7.52. A large low-field shift observed in going from **8** to **17** is attributed to the inductive effect of the positively-charged 1,3-benzodithiolylium nuclei. The high-field doublet of **17** can be assigned to the C-4 H of the pyrrole ring because the influence of the dithiolylium nuclei is less at this position. For the same reason, the pair of doublets of **29** at δ 6.66(J=5 and 3 Hz) can be assigned to the C-4 H of the pyrrole rings. The coupling constant between the C-3 H and C-4 H is 5 Hz for **17**. Therefore, the pair of doublets of **29** at δ 7.69 (J=5 and 1 Hz) and δ 7.88(J=3 and 1 Hz) can be assigned to C-3 H and C-5 H, respectively. The appearance of the benzene-ring proton signal of the 1,3-dithiolylium nuclei of **17** an **15b** as a typical AA′XX′ pattern symmetrical about its center indicates that the conjugation between the two rings is not strong enough to hinder free rotation about the pinch bond. The same holds true for **29** since the dithiolylium-ring proton signal appears as a sharp singlet at δ 8.56. However, the chemical-shift value of δ 8.56, when compared to the value of δ 8.66 observed for the ring protons of **28** in deuteriofluoroacetic acid, suggests a significant contribution of structure **29′** to the ground state of

Table 1. NMR data

Compound	Solvent	δ (ppm) with TMS as internal reference
8	CDCl$_3$	6.07 (2H, d, J=2.6 Hz, pyrrole ring), 6.26 (2H, s, methine), 6.9—7.2 (8H, 2AA′BB′ m, benzene ring), 8.8 (1H, very broad m, NH)
17	CF$_3$CO$_2$D	6.02 (1H, s, methine), 6.78 (1H, d, J=5 Hz, 4-C H of pyrrole ring), 7.52 (1H, d, J=5 Hz, 3-C H of pyrrole ring), 7.0—7.4 (4H, AA′BB′ m, benzene ring protons of benzodithiol-2-yl group), 7.7—8.3 (4H, AA′XX′ m, benzodithiolylium nucleus)
18	CDCl$_3$	6.06 (1H, s, methine), 6.65 (1H, d, J=4 Hz, 7-C H), 6.9—7.7 (9H, m, 8-C H + benzene ring protons)
7	CDCl$_3$	6.0—6.2 (2H, complex m, 3- and 4-C H's of pyrrole ring), 6.32 (1H, s, methine) 6.58 (1H, m, 5-C H of pyrrole ring), 6.9—7.3 (4H, AA′BB′ m, benzene ring), 8.5 (1H, broad m, NH)
15b	DMSO-d_6	6.80 (1H, dd, J=5 and 3 Hz, 4-C H of pyrrole ring), 7.7—8.0 (3H, 3-C H + half of AA′XX′ m of benzene ring protons), 8.10 (1H, dd, J=3 and 1 Hz, 5-C H), 8.3—8.6 2H, m, half of AA′XX′ m)
25	CDCl$_3$	6.55 (1H, d, J=5 Hz, 7-C H), 7.05—7.65 (5H, m, 8-C H + benzene ring protons), 7.71 (1H, s, 6-C H)
29	DMSO-d_6	6.66 (1H, dd, J=5 and 3 Hz, 4-C H), 7.69 (1H, dd, J=5 and 1 Hz, 3-C H), 7.88 (1H, dd, J=3 and 1 Hz, 5-C H), 8.56 (2H, s, dithiolylium nucleus)
2a	CCl$_4$	6.40 (1H, d, J=4 Hz, 7-C H), 6.78 (2H, s, dithiole ring), 6.94 (1H, d, J=4 Hz, 8-C H), 7.52 (1H, s, 6-C H)
	CH$_3$CN	6.54 (1H, d, J=4 Hz, 7-C H), 7.23 (2H, s, dithiole ring), 7.16 (1H, d, J=4 Hz, 8-C H), 7.58 (1H, s, 6-C H)
9	CDCl$_3$	2.16 (3H, s, 5-C methyl), 2.18 (3H, s, C-2 methyl), 6.08 (1H, d, J=2.5 Hz, C-4 H of pyrrole ring), 6.40 (1H, s, methine), 6.9—7.3 (4H, AA′BB′ m, benzene ring), 7.45 (1H, broad m, NH)
20b	DMSO-d_6	2.22 (3H, s, 5-C methyl), 2.62 (3H, s, 2-C methyl), 6.55 (1H, broad s, 4-C H), 7.7—8.5 (4H, AA′XX′ m, benzodithiolylium nucleus)
27	CDCl$_3$	2.17 (3H, broad s, 7-C methyl), 2.40 (3H, s, 5-C methyl), 5.95 (1H, broad s, 8-C H), 7.1—7.6 (4H, complex m, benzene ring)
22	DMSO-d_6	2.45 (3H, s, 5-C methyl), 2.72 (3H, s, 2-C methyl), 7.42 (1H, s, methine), 7.0—7.6 (4H, AA′BB′ m, benzene ring protons of benzodithiol-2-yl group), 7.7—8.7 (4H, AA′XX′ m, benzodithiolylium nucleus)
23	CDCl$_3$	2.47 (3H, s, methyl), 2.52 (3H, s, methyl), 6.8—7.7 (9H, m, benzene ring protons + methine proton)
30	DMSO-d_6	2.23 (3H, broad s, 5-C methyl), 2.55 (3H, s, 2-C methyl), 6.48 (1H, broad s, 4-C H), 8.49 (2H, s, dithiolylium ring)
3b	CDCl$_3$	2.15 (3H, broad s, 7-C methyl), 2.32 (3H, s, 5-C methyl), 5.86 (1H, broad s, 8-C H), 6.73 (2H, s, dithiole ring)
	CH$_3$CN	6.05 (1H, broad s, 8-C H), 7.10 (2H, s, dithiole ring)
	(CH$_3$)$_2$CO	5.95 (1H, broad s, 8-C H), 7.23 (2H, s, dithiole ring)

29, since **28′** is known to contribute significantly to the ground state of **28**.[11)]



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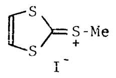

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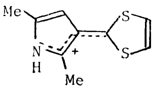

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The formation of dithiolylium salt **20b** from **9** was also accompanied by a large low-field shift of the pyrrole-ring protons. The singlet due to the C-2 methyl of the pyrrole ring of **20b** is shifted to lower field by 0.44 ppm compared the that of **9**, whereas the singlet due to the C-5 methyl, which is broadened by long-range coupling with the C-4 H, is shifted to lower field by only 0.06 ppm and the broad singlet due to the C-4 H to lower field by only 0.47 ppm. This indicates that structure **30′** contributes significantly to the ground state of **30**. The chemical shift value of δ 8.49 of the dithiolyium-ring proton signal of **30** is also indicative of the contribution of **30′** as described for **29**. Free rotation about the pinch bond also occurs in this case.

In azadithiafulvalene **18**, the doublet at δ 6.65 can be assigned to the C-7 H (the C-8 H signal was obscured by signals due to the benzene-ring protons), which is less influenced than is the C-8 H by the electronegative nitogen atom and hence is expected to resonate at a higher value of the field than the C-8 H. The coupling constant between the C-7 H and C-8 H is 4 Hz in **18**. Accordingly, the doublet of **25** at δ 6.55 (J=4 Hz) and that of **2a** at δ 6.40 (J=4 Hz) can be assigned to the C-7 H, the doublet of **2a** at δ 6.94 (J=4 Hz) to the C-8H, and the singlet of **25** at δ 7.71 and that of **2a** at δ 7.52 to the C-6 H. The dithiole-ring proton signals of **2a** and **3b** appear as a singlet at δ 6.78 in carbon tetrachloride and at δ 6.73 in deuteriochloroform. This may be due to accidental equivalence of the two protons rather than rotation about the pinch bond. Evidence for this description comes from the fact that the benzene-ring proton signals of **25** and **27** appear as a complex multiplet, but not as a symmetrical AA′BB′ pattern. The chemical-shift values of δ 6.78 and 6.73 of the dithiole-ring proton signals of **2a** and **3b** are slightly lower than the reported value (δ 6.60) of the dithiole-ring protons of 1,4-dithiafulvalene (**4**),[3)] thus suggesting that the contribution of a dipolar structure is somewhat larger in **2a** and **3b** than in **4** due to the influence of the electronegative nitrogen atom. Here, of particular interest, is the large solvent effect observed with **2a** and **3b**. The dithiole-ring proton signals of **2a** were shifted to lower field by 0.45 ppm upon changing the solvent from carbon tetrachloride to acetonitrile, the other protons also being shifted to lower field (0.06 ppm for C-6 H, 0.22 ppm for C-7 H, and 0.14 ppm for C-8 H). The dithiole-ring protons of **3b** were also shifted to lower field by 0.37 and 0.50 ppm upon changing the solvent from deuteriochloroform to acetonitrile and acetone, respectively. This may be ascribed to the increased contribution of dipolar structures, such as **2′** and **3′**, in the polar solvents. A contribution from a dipolar structure increases the dithiolylium character of the dithiole ring of **2** and **3**, and the ring-current effect induced by the aromatic sextet formed in both rings may result in a shift to lower field. However, the possibility cannot be excluded that this low-field shift is the result of charge-transfer interactions of **2a** and **3b** with the solvent molecules, in which **2a** and **3b** serve as electron donors and acetonitrile or acetone as electron acceptors. UV data for dithiolylium salts, **29** and **30**, and azadithiafulvalenes, **2a** and **3b**, are listed in Table 2. The resemblance of the spectral features of **29** and **2a** probably reflects the similarity between the electronic structures of both compounds. On the other hand, conversion of **30** to **3b** resulted in a considerable change in spectral features. Changing the solvent from carbon tetrachloride to acetonitrile causes a slight bathochromic shift of the longest absorptions of **2a** and **3b**, probably because these strong absorptions are π-π^* transitions and, therefore, the more polar excited states are more stabilized in the polar solvent than are the ground states.

TABLE 2. UV DATA

Compound	Solvent	λ_{max} (nm) (log ε)
29	CH_3CN	440 (4.46), 424 (4.50), 247 (4.27)
2a	CCl_4	441 (4.19), 421 (4.19), 400sh (3.93), 320sh (2.74)
	CH_3CN	443 (4.47), 423 (4.40), 404sh (4.13), 312 (2.57)
30	CH_3CN	418(4.29), 350(3.85), 246(4.26)
3b	CCl_4	393 (*ca.* 3.7), 380 (*ca.* 3.6)[a)]
	CH_3CN	396 (*ca.* 4.0)[a)]

a) Accurate log ε values could not be obtained because of the instability of the sample in solutions.

Experimental

2-Isopentoyloxy-1,3-benzodithiole (**6**),[12)] 2-(1,3-benzodithiol-2-yl)-, 2,5-bis(1,3-benzodithiol-2-yl)-, and 2,5-dimethyl-3-(1,3-benzodithol-2-yl)pyrroles (**7**, **8**, and **9**),[5)] trityl tetrafluoroborate (**10**),[13)] 1,3-benzodithiolylium tetrafluoroborate (**14**),[6)] 2-methylthio-1,3-benzodithiolylium perchlorate (**24**),[8)] and 2-methylthio-1,3-dithiolylium iodide (**28**)[9)] were prepared by methods in the literature. Acetonitrile was refluxed and distilled from calcium hydride, and stored over molecular sieves. Ether was distilled and dried over molecular sieves.

Reaction of ***7*** *with* ***10***. To a stirred and ice-cooled solution of **7** (1.10 g; 5 mmol) in dry acetonitrile (15 ml) was added dropwise a solution of **10** (1.65 g; 5 mmol) in dry acetonitrile (10 ml) over a period of 20 min. Stirring was continued for 0.5 h while the mixture was brought to room temperature. The resulting precipitate was collected by filtration, washed with acetonitrile (10 ml), and dried to give 0.61 g (44%) of 2,5-ditritylpyrrole (**13**). The combined filtrate and washings were evaporated and the residue was subjected to silica gel column chromatography. Elution with carbon tetrachloride gave additional **13** (0.14 g; 10%). **13**; mp 229—230 °C (from benzene), colorless granules, IR (Nujol) 3400 cm^{-1} (NH), NMR ($CDCl_3$) δ 5.87 (2H, d, J=*ca.* 2.6 Hz) and 7.0—7.3 (30 H, m). Found: C, 91.42; H, 5.97; N, 2.31%. Calcd for $C_{42}H_{33}N$: C, 91.43; H, 6.03; N, 2.54%.

To a stirred and ice-cooled solution of **7** (1.10 g; 5 mmol) in acetonitrile (15 ml) was added dropwise an acetonitrile solution (10 ml) of **10** (3.30 g; 10 mmol) over a period of 25 min. The ice bath was removed and the mixture was stirred for 1 h. The precipitate was filtered, washed with acetonitrile, and dried to give 1.32 g (48%) of **13**. Triethylamine (2 ml) was added to the dark reddish-brown filtrate and the mixture was evaporated. The residue was subjected to chromatography on silica gel. Elution with carbon tetrachloride gave triphenylmethane (0.32 g), dibenzotetrathiafulvalene (**16**) (0.02 g; 2%), mp and mixed mp with an authentic specimen[6] 236—237 °C, **13** (0.39 g; 14%), and trityl alcohol (0.43 g).

*2,5-Ditritylpyrrole (13) from **10** and Pyrrole.* To a stirred and ice-cooled solution of pyrrole (0.34 g; 5 mmol) in 15 ml of acetonitrile was added dropwise a solution of **10** (3.30 g; 10 mmol) in 20 ml of acetonitrile over a period of 0.5 h. A white solid began to precipitate during the addition. The mixture was stirred for 1.5 h at room temperature and then 2 ml of triethylamine was added. The precipitate was collected, washed with acetonitrile, and dried, yielding 1.95 g (71%) of **13**, mp 229—230 °C, undepressed on admixture with the products from **7** and **10**.

2-[5-(1,3-Benzodithiol-2-yl)-2-pyrrolyl]-1,3-benzodithiolylium Tetrafluoroborate (17). A solution of **10** (3.9 g; 12 mmol) in 25 ml of acetonitrile was added dropwise to a stirred and ice-cooled suspension of **8** (3.72 g; 10 mmol) in acetonitrile (80 ml) over a period of 20 min. The mixture was warmed to room temperature for 20 min and stirred for an additional 45 min. Ether (150 ml) was added to the mixture to precipitate the product. The precipitate was collected and washed with ether to give 2.32 g (51%) of **17** as yellowish-brown crystals. This was purified by dissolution in acetonitrile and reprecipitation with ether (attempted recrystallization from several solvents produced tarry materials). **17**; mp 179—180 °C (dec.), IR (Nujol) 3405 (NH) and 1000—1100 cm^{-1} (BF_4^-). Found: C, 46.50; H, 2.63; N, 2.87%. Calcd for $C_{18}H_{12}NS_4BF_4$: C, 47.27; H, 2.64; N, 3.06%.

6-(1,3-Benzodithiol-2-yl)-2,3-benzo-5-aza-1,4-dithiafulvalene (18). Triethylamine (1.5 ml) was added with stirring to an ice-cooled solution of **17** (1.08 g; 2.4 mmol) in acetonitrile (30 ml). Immediately, a yellow precipitate of **18** was separated out, which was then collected and washed with acetonitrile to give 0.85 g (98%) of **18**, which melted at 147—151 °C (decomp.). The crude material gave satisfactory results upon elemental analysis. Found: C, 58.50; H, 3.06; N, 3.79; S, 34.39%. Calcd for $C_{18}H_{11}NS_4$: C, 58.54; H, 3.00; N, 3.79; S, 34.66%.

***17** from **18** by Treatment with Tetrafluoroboric Acid.* **18** (185 mg; 0.5 mmol) was added with stirring to 4 ml of ice-cooled tetrafluoroboric acid. The mixture was stirred for 0.5 h at 0 °C. The yellowish-brown precipitate of **17** was filtered, washed with ether, and dried. It weighed 222 mg (97%).

*Reaction of **9** and **10**.* To a stirred and ice-cooled solution of **9** (1.24 g; 5 mmol) in 15 ml of acetonitrile was added dropwise a solution of **10** (1.65 g; 5 mmol) in 15 ml of acetonitrile over a period of 25 min. Stirring was continued for 2.5 h while the mixture was brought to room temperature. The precipitate was collected by filtration to give 0.5 g of a brown solid. The filtrate was diluted with 200 ml of ether and filtration of the resulting precipitate gave an additional 0.7 g of the brown solid; the IR spectrum of the solid had characteristic absorptions due to NH and BF_4^- groupings (3200 and 1000—1100 cm^{-1}), but did not result in a pure material upon repeated recrystallization. The filtrate was evaporated. The residue along with the brown solid from the reaction mixture were subjected to chromatography on silica gel. Elution with carbon tetrachloride gave 0.68 g of triphenylmethane, 0.50 g (17%) of 2,5-dimethyl-3-(1,3-benzodithiol-2-yl)-4-tritylpyrrole (**19**), and small amounts of a few unidentified products. **19**; mp 258—261 °C (dec.) (from benzene), colorless granules, IR (Nujol) 3360 cm^{-1} (NH). Found: C, 78.52; H, 5.55; N, 2.72%. Calcd for $C_{32}H_{27}NS_2$: C, 78.51; H, 5.56; N, 2.86%.

*Reaction of **9** with **14**.* 1.44 g (6 mmol) of **14** dissolved in 15 ml of acetonitrile was added dropwise to a stirred and ice-cooled suspension of 1.23 g (5 mmol) of **9** in 15 ml of acetonitrile over a period of 15 min. Stirring was continued for 2 h while the mixture was brought to room temperature. Filtration of the resulting precipitate and washing with acetonitrile gave 0.71 g (36%) of **21**. Ether (250 ml) was added to the brown filtrate and the precipitate was filtered to give 0.68 g of orange crystals which melted at 186—192 °C (dec). NMR analysis showed that the precipitate consisted of **20a** and **22** in a ratio of *ca.* 4:3 (in 20 and 15% yield, respectively). 2,5-Dimethyl-3,4-bis(1,3-benzodithiol-2-yl)pyrrole (**21**); mp 242—245 °C (dec) (from benzene), faint pale yellow granules, IR (Nujol) 3350 cm^{-1} (NH). Found: C, 60.45; H, 4.34; N, 3.15%. Calcd for $C_{20}H_{17}NS_4$: C, 60.11; H, 4.29; N, 3.51%.

***21** from **6** and 2,5-Dimethylpyrrole.* 2,5-Dimethylpyrrole (0.48 g; 5 mmol) and **6** (2.40 g; 10 mmol) were dissolved in 10 ml of acetic acid. The mixture was allowed to stand at room temperature overnight. The resulting crystalline precipitate was filtered and washed with methanol. The near-white solid weighed 1.86 g (93%), mp 242—245 °C (dec), undepressed upon admixture with a specimen from **9** and **14**.

2-[2,5-Dimethyl-4-(1,3-benzodithiol-2-yl)-3-pyrrolyl]-1,3-benzodithiolylium Tetrafluoroborate (22). To a suspension of **21** (1.67 g; 4.2 mmol) in acetonitrile (25 ml) was added dropwise a solution of **14** (1.44 g; 6 mmol) in 15 ml of acetonitrile over a period 20 min. The mixture was stirred overnight and the resulting precipitate was filtered and washed with ether to give 1.06 g (52%) of **22**. Dilution of the filtrate with ether (150 ml) gave additional **22** (0.48 g; 24%). **22**: mp 223—226 °C (dec) (from acetonitrile), orange needles, IR (Nujol) 3250 (NH) and 1000—1100 cm^{-1} (BF_4^-). Found: C, 49.52; H, 3.35; N, 2.80; S, 26.79%. Calcd for $C_{20}H_{16}NS_4BF_4$: C, 49.48; H, 3.32; N, 2.89; S, 26.42%.

5,7-Dimethyl-8-(1,3-benzodithiol-2-yl)-2,3-benzo-6-aza-1,4-dithiafulvalene (23). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.5 ml) was added with stirring to an ice-cooled suspension of formation of **22** (0.20 g; 0.41 mmol) in 10 ml of acetonitrile. Immediately, a bright orange precipitate of **23** appeared with the disappearance of **22**. Filtration of the precipitate and washing with acetonitrile (5 ml) gave 0.15 g (92%) of **23**, mp 204—209 °C (dec), which gave satisfactory results upon elemental analysis without further purification. Found: C, 60.55; H, 3.99; N, 3.51%. Calcd for $C_{20}H_{15}NS_4$: C, 60.45; H, 3.81; N, 3.53%.

2-(2-Pyrrolyl)-1,3-benzodithiolylium Perchlorate (15b). Salt **24** (0.60 g; 2 mmol) was added in small portions to a stirred solution of pyrrole (134 mg; 2 mmol) in acetonitrile (20 ml). The mixture was stirred for 3 days. The precipitate was filtered, washed with ether, and dried to give 0.53 g (84%) of **15b**, mp>230 °C (dec) (from acetonitrile-ether), yellowish-brown needles. Found: C, 41.61; H, 2.54; N, 4.47; S, 20.28%. Calcd for $C_{11}H_8NS_2ClO_4$: C, 41.57;

H, 2.54; N, 4.41; S, 20.18%.

*2-(2,5-Dimethyl-3-pyrrolyl)-1,3-benzodithiolylium Perchlorate (**20b**).* A mixture of **24** (0.60 g; 2 mmol) and 2,5-dimethylpyrrole (0.19 g; 2 mmol) was stirred overnight at room temperature. The precipitate was filtered, washed with ether, and dried to give 0.35 g (51%) of **20b**. Dilution of the filtrate and collection of the resulting precipitate gave another crop of **20b** (0.12 g; 16%). **20b**; mp 225—227 °C (from acetonitrile), yellow needles, IR (Nujol) 3200 $\mathrm{cm^{-1}}$ (NH). Found: C, 45.14; H, 3.50; N, 4.07; S, 18.77%. Calcd for $C_{13}H_{12}NS_2ClO_4$: C, 45.15; H, 3.50; N, 4.05; S, 18.54%.

*2-(2-Pyrrolyl)-1,3-dithiolylium Iodide (**29**).* A mixture of pyrrole (0.27 g; 4 mmol) and **28** (1.10 g; 4 mmol) in acetonitrile (40 ml) was stirred for 2 days at room temperature. The precipitate was collected, washed with ether, and dried to give 1.08 g (92%) of **29**, mp 190—191 °C (dec) (from acetonitrile) yellowish-brown scales, IR (KBr), 3050, 1550, 1425, 1400, 1140, 1050, and 862 $\mathrm{cm^{-1}}$. Found: C, 28.54; H, 2.05; N, 4.35; S, 21.71%. Calcd for $C_7H_6INS_2$: C, 28.48; H, 2.05; N, 4.75; S, 21.73%.

*2-(2,5-Dimethyl-3-pyrrolyl)-1,3-dithiolylium Iodide (**30**).* 2,5-Dimethylpyrrole (0.57 g; 6 mmol) and **28** (1.66 g; 6 mmol) was stirred in 40 ml of acetonitrile at room temperature for 2 days. The precipitate was filtered, washed with acetonitrile, and dried to give 1.60 g (83%) of **30**, mp 214—219 °C (dec) (from acetonitrile), yellowish-brown needles, IR (KBr) 3050, 2980, 1605, 1430, 1350, 1260, 1020, 920, 780, 725, and 710 $\mathrm{cm^{-1}}$. Found: C, 33.46; H, 3.09; N, 4.48; S, 19.80%. Calcd for $C_9H_{10}INS_2$: C, 33.44; H, 3.12; N, 4.33; S, 19.84%.

*2,3-Benzo-5-aza-1,4-dithiafulvalene (**25**) and Its Charge-transfer Salt, **26**, with DDQ.* DBU (0.2 ml) was added to a stirred and ice-cooled suspensin of **15b** (0.20 g; 0.6 mmol) in acetonitrile (10 ml). Immediately, the formation of a yellow precipitate of **25** occurred with the disappearance of **15b**. After 5 min, the precipitate was filtered quickly, washed with acetonitrile, and dried to give 40 mg (31%) of **25**, mp>130 °C (dec) Found: C, 60.81; H, 3.25; N, 6.15; S, 29.54%. Calcd for $C_{11}H_7NS_2$: C, 60.83; H, 3.25; N, 6.45, S, 29.47%. DDQ (*ca.* 0.2 g) was added to the combined filtrate and washings. The resulting dark violet precipitate was filtered, washed with methanol, and dried to give 163 mg (37%) of **26**, which melted at 225—226 °C (dec). IR (Nujol) 2200 (CN), 1570, and 1550 $\mathrm{cm^{-1}}$. Found: C, 50.80; H, 1.87; N, 9.11%. Calcd for $C_{19}H_7O_2Cl_2N_3S_2$: C, 51.35; H, 1.59; N, 9.46%.

*5,7-Dimethyl-2,3-benzo-6-aza-1,4-dithiafulvalene (**27**).* DBU (0.2 ml) was added to a stirred and ice-cooled suspension of **20b** (173 mg; 0.5 mmol) in 6 ml of acetonitrile. The precipitate was filtered after 5 min, washed with acetonitrile, and dried to give 83 mg (68%) of **27** as orange crystals, which melted at 182—185 °C (dec). Found: C, 63.50; H, 4.54; N, 5.70; S, 25.64%. Calcd for $C_{13}H_{11}NS_2$: C, 63.67; H, 4.52; N, 5.71; S, 26.10%.

*5-Aza-1,4-dithiafulvalene (**2a**).* DBU (0.5 ml) was added with stirring to an ice-cooled suspension of **29** (0.40 g; 1.36 mmol) in 7 ml of acetonitrile. Immediately, the mixture turned dark red with the disappearance of **29**. After 10 min, the mixture was diluted with 100 ml of ether, washed with saturated an aqueous sodium chloride solution (50 ml × 5), and dried. Evaporation of the ether left a red oily residue, to which hexane (10 ml) was added. It was allowed to stand in a refrigerator for 2 days. The oil crystallized, and was filtered and washed with hexane to give 0.18 g (82%) of **2a** as orange needles, which melted at 85—87 °C. IR (KBr) 1538, 1500, 1355, 1012, 842, and 740 $\mathrm{cm^{-1}}$. Found: C, 50.21; H, 3.05; N, 8.26; S, 38.15%. Calcd for $C_7H_5NS_2$: C, 50.31; H, 3.02; N, 8.38; S, 38.30%.

*5,7-Dimethyl-6-aza-1,4-dithiafulvalene (**3b**).* To a stirred and ice-cooled suspension of **30** (323 mg; 1 mmol) was added DBU (0.2 ml). Immediately, the mixture turned red with the disappearance of **30** and the separation of an orange precipitate. After 10 min, the precipitate was filtered, washed with acetonitrile, and dried to give 117 mg (70%) of **3b** as orange crystals, which melted at 105—109 °C (dec). IR (KBr) 2920, 1535, 1475, 1315, 1270, 1000, 980, and 700 $\mathrm{cm^{-1}}$. Found: C, 55.17; H, 4.64; N, 6.88; S, 32.71%. Calcd for $C_9H_9NS_2$: C, 55.38; H, 4.65; N, 7.18; S, 32.79%. The addition of tetracyanoquinodimethane (TCNQ) (*ca.* 0.1 g) to the filtrate gave a small amount of a greenish-black precipitate, which was assumed to be a charge-transfer salt of **3b** and TCNQ.

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