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# ALKYLTHIO-SUBSTITUTED (AZA)FULVALENES

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**Abstract**- Bis-methylthio-5-aza-1,4-dithiafulvalenes (5-7) and bis-methylthio-2-azacalicenes (9,10), resp., are formed when pyrroles and indole are reacted with tris-methylthio-1,3-dithiolium tetrafluoroborate and tris-methylthio-cyclopropenylium tetrafluoroborate, resp., the latter readily prepared from tetrachlorocyclopropene and dimethylmethylthiosulfonium tetrafluoroborate. Poly-alkylthio-dithiafulvalenes (12,13) and their 5,8-diaza derivatives can be generated through the condensation of pentakis-methylthio-cyclopentadiene and tris-ethylthio-imidazole, resp., with dithiolium salts.

The discovery of the high electrical conductivity of the TTF-TCNQ complex[1] in 1973 stimulated an intensive search for new donor molecules that are easy to oxidize.[2-8] Target molecules in particular were analogues of TTF, i.e., heterocyclic compounds isoelectronic with heptafulvalene.[9] Systems isoelectronic with sesquifulvalene were paid little attention, presumably since they are expected to be less prone to oxidation than the heptafulvalene derivatives. However, this drawback could be compensated for, at least partially, by donor groups. Dialkylamino and alkylthio groups have strong electron-releasing properties. Regarding "organic metals", compounds carrying alkylthio groups appear to be advantageous. Alkylthio-substituted tetrathiafulvalenes even give rise to materials with superconductivity.[10]

The method of choice for the synthesis of sulfur derivatives of sesquifulvalene is the condensation of dithiolium salts with cyclopentadienes and their heterocyclic derivatives (pyrroles, indoles, imidazoles, pyrazoles).[11-20] The parent compound, 1,3-dithiafulvalene,[11] has been prepared in this way and a number of its aza derivatives as well.[14,15] There is no report, however, on the synthesis of donor-substituted azadithiafulvalenes and related compounds.

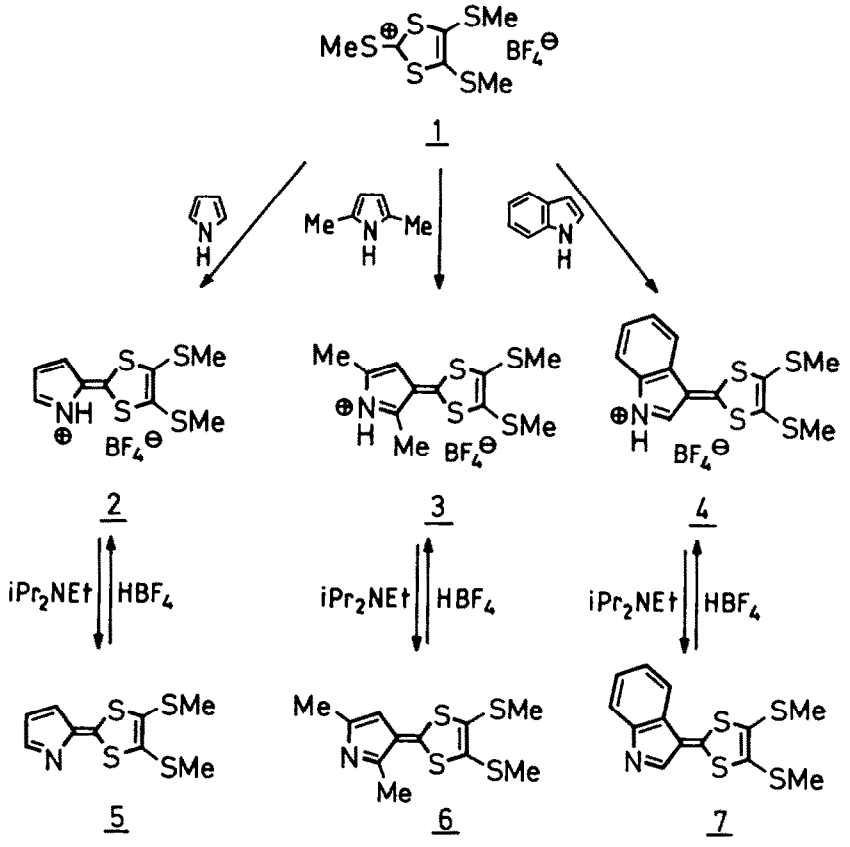
## Bis-methylthio-5-aza-1,4-dithiafulvalenes

Pyrrole, 2,5-dimethylpyrrole and indole readily react in acetonitrile with tris-methylthio-1,3-dithiolium tetrafluoroborate (1) to afford the azadithiafulvalenium tetrafluoroborates 2-4 in high yields. Their deprotonation with Hünig's base delivers the azadithiafulvalenes 5 and 7 in pure form; 6 could be obtained only in solution.

The $^1$H NMR spectrum of 5 (Table 2) resembles the spectra of 5-aza-1,4-dithiafulvalene and its 2-phenyl derivative[14-16] indicating that the charge

distribution in azadithiafulvalenes is virtually independent from substituents in the dithiole ring.

The UV/VIS spectra of the salts 2-4 reveal a bathochromic shift of the longest-wavelength absorption as compared with compounds without substituents or a




phenyl group in the dithiole ring. The color of the neutral azadithiafulvalenes, however, shows almost no substituent effect (Table 1).

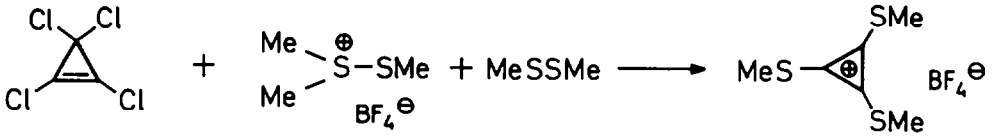
**Table 1** Longest-wavelength absorption maxima of 5-aza-1,4-dithiafulvalenes (in acetonitrile)

| R, R' | $\lambda_{max}$ (nm) | $\lambda_{max}$ (nm) |
|---|---|---|
| H, H (ref. 16a) | 440 | 423 |
| H, Ph (ref. 15) | 450 | 456 |
| SMe, SMe | 473 | 446 |

### Bis-methylthio-2-azacalicenes

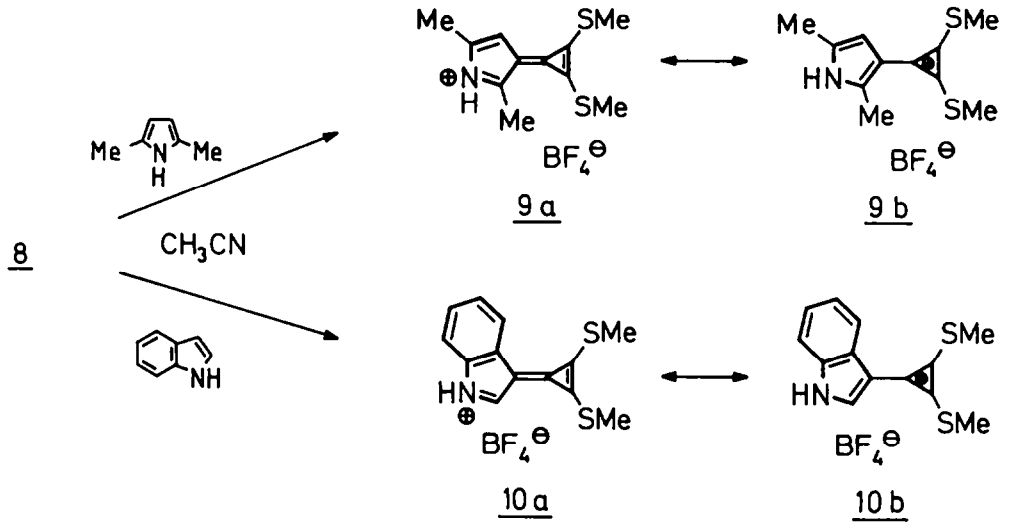
Salts of benzoazacalicenes were first described in 1966.[21] Salts of azacalicenes could be deprotonated and the free azacalicenes characterized through their UV/VIS spectra.[14] Donor-substituted calicenes have been prepared only

recently.[22] The method used for the synthesis of 2-4 is expected to be also applicable for the synthesis of bis-methylthio-substituted azacalicenes, when instead of 1 a tris-methylthio-cyclopropenylium salt is used. The syntheses developed for these latter salts[23-27] have some drawbacks, however (modest yields, use of expensive silver salts, oxidizing properties of the counter-ion hexachloroantimonate). The reaction of tetrachlorocyclopropene with dimethyl-methylthiosulfonium tetrafluoroborate[28] now makes tris-methylthio-cyclo-propenylium tetrafluoroborate 8 readily available (70%). Reaction of 8 with




8

2,5-dimethylpyrrole or indole gives rise to the 2-azacalicenium salts 9 and 10. Attempts to prepare the azacalicenes from their salts failed.

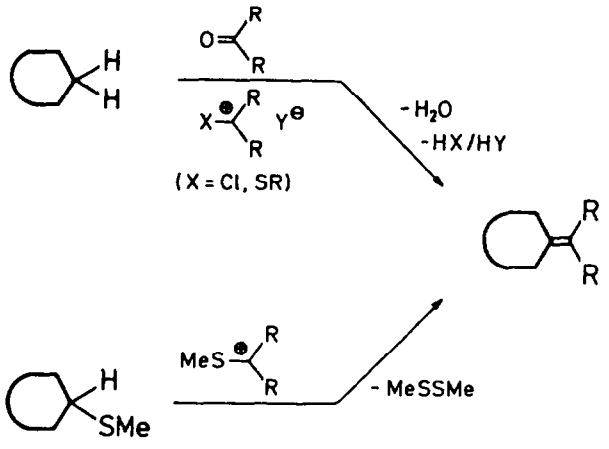



The $^1$H NMR spectra of 9 and 10 (Table 2) resemble those of 3 and 4. The signals of the vinylic protons of the hetero rings in the spectra of 9 and 10, however, appear at higher field than those in the spectra of 3 and 4, and it must be therefore concluded that the resonance structures B dominate in the ground states of 9 and 10. In contrast to this result, in the salts of triphenyl-1-aza- and -2-azacalicenes the pyrrolium resonance structures dominate,[14] which demonstrates the strong donor effect of the methylthio groups in 9 and 10.

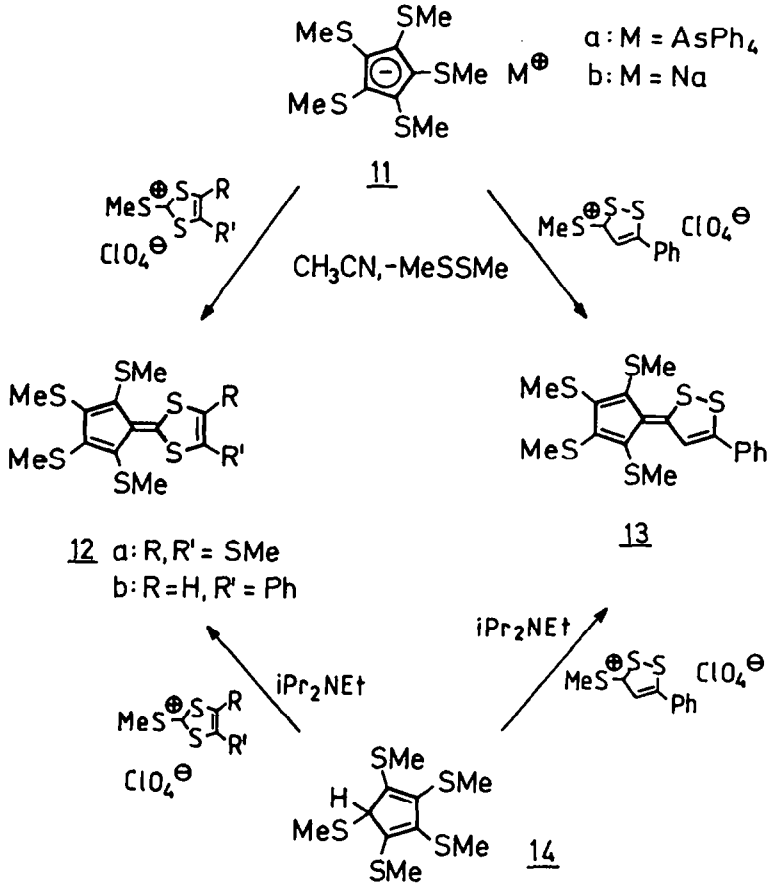
## Poly-methylthio-(aza)dithiafulvalenes

Fulvalenes (and fulvenes) may be generated through the condensation of cyclopentadienes and related compounds with (thio)carbonyl compounds or with the corresponding carbenium salts (Scheme 1). A novel method for the synthesis

Scheme 1



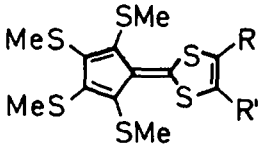

of donor-substituted fulvalenes utilizes methylthiocyclopentadienes and methylthiodithiolium salts as starting materials. The final step in this reaction is the elimination of dimethyldisulfide instead of water or an acid in the conventional procedures. The salts 11 of pentakis-methylthio-cyclopentadiene (14) have been synthesized recently in an elegant way.[29] Upon addition of 3-methylthio-1,2- and 2-methylthio-1,3-dithiolium salts to solutions of 11 in

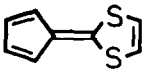


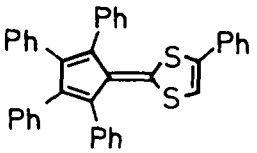
acetonitrile the polymethylthio-dithiafulvalenes 12 and 13 were obtained in fair yields. Instead of 11 (yields are better with 11a, but it must be prepared in moderate yield from 11b), 14[30] can also be employed in the presence of Hünig's base.

The formation of 12,13 from 11,14 has some precedents in the literature. Electrochemical dimerization of 1 (cf. the reduction of other 2-methylthio-1,3-dithiolium salts with zinc[31]) gives rise to a hexakis-methylthio-dihydrotetrathiafulvalene which upon heating in carbontetrachloride eliminates dimethyldisulfide to afford tetrakis-methylthiotetrathiafulvalene.[31] A related reaction in the 1,2-dithiole series has also been reported[33] and bipyranylidenes are formed through cathodic reduction of thiopyrones in the presence of alkyl halides.[34] It is the advantage of the method described here that unsymmetrical fulvalenes are obtained and that the anionic and the cationic components can be varied. The only method that fulfils these requirements too but seems to be restricted to benzo-TTF's is the reaction of lithium methylthiobenzodithiole with isotrithiones.[35]

The absorption maxima in the UV/VIS spectra of 12 appear at longer wavelengths as those of 1,4-dithiafulvalene.[11] This bathochromic effect is caused

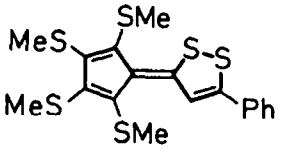


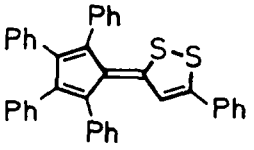




12 a: R,R' = SMe
b: R = H,R' = Ph

$\lambda_{max}$ 490 nm 418 nm 455 nm



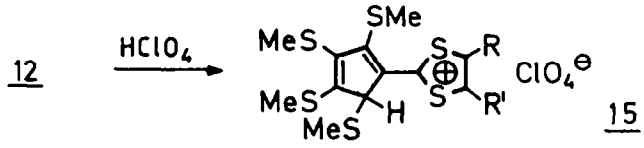




13

$\lambda_{max}$ 542 nm 508 nm

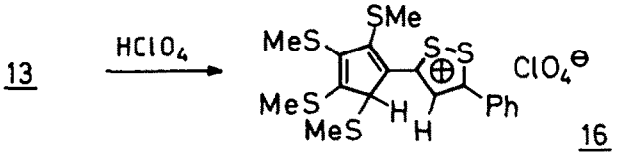
by the methylthio groups in the cyclopentadiene ring as is demonstrated by the comparison of 12b with pentaphenyl-1,4-dithiafulvalene.[13] An analogous bathochromic shift is observed in the case of 13 as compared with 3,5,6,7,8-pentaphenyl-1,2-dithiafulvalene.[12]

Sesquifulvalenes and heterosesquifulvalenes are rather strong π-bases and are protonated in the α-position of the cyclopentadiene ring.[12,13,36] Accordingly, 12a on treatment with perchloric acid affords dark blue crystals



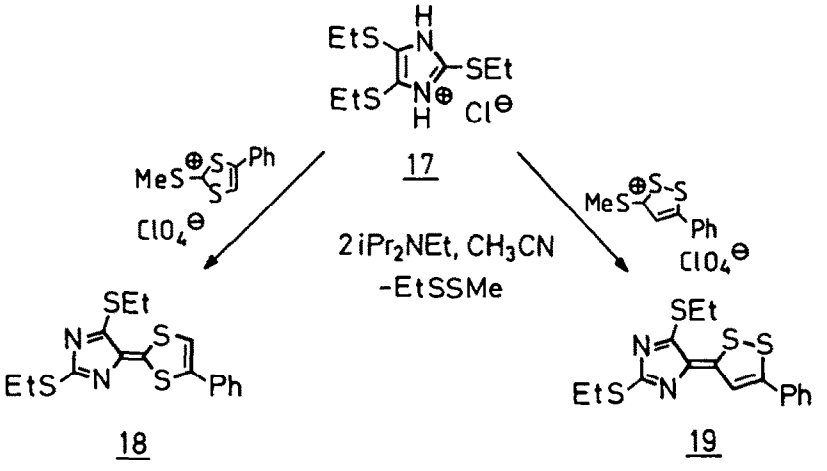

a: R,R' = SMe
b: R = Ph,R' = H

of 15a in 63% yield. The salts 15b and 16 , formed on addition of perchloric acid or trifluoroacetic acid to acetonitrile solutions of 12b and 13, respectively, can be characterized through their UV/VIS spectra (Table 2). The color




of 15 and 16 is in accordance with the trimethine cyanine nature (cf.[37,38]) of these salts.

The same type of condensation as with 14 occurs when tris-methylthio-imidazole hydrochloride 17 is reacted with 2-methylthio-4-phenyl-1,3-dithiolium tetrafluoroborate or 3-methylthio-5-phenyl-1,2-dithiolium tetrafluoroborate in the presence of Hünig's base. The new diazadithiafulvalenes 18 and




19 are formed in 50-60% yield. The bathochromic shift (cf. Table 2) of the 1,2-dithiole derivative 19 as compared with the 1,3-dithiole 18 (535 vs 468 nm) is even larger than in the case of 13/12b (542 vs 490 nm). In contrast to 12 and 13, the effect of the methylthio groups in 18 and 19 is about the same as that of phenyl groups (cf. 3,6,8-triphenyl-5,7-diaza-1,2-dithiafulvalene: $\lambda_{max}$ = 540 nm[14]).

**Table 2** Spectroscopic data of 2-10, 12, 13, 15, 16, 18 and 19

**A**: $^1$H-NMR (60 MHz)/**B**: $^{13}$C-NMR (80 MHz) [δ (ppm)]
**C**: IR (KBr) [ν ($cm^{-1}$)] **D**: UV/VIS ($CH_3CN$) [$\lambda_{max}$ (nm), (lg ε)]

2 **A** (in DMF-$d_7$): 2.77 (s; 6 H, $SCH_3$), 6.65 (dd, $J_{7,8}$ = 4.5 Hz, $J_{6,7}$ = 2.2 Hz; 1 H, H-7), 7.65 (dd, $J_{7,8}$ = 4.5 Hz, $J_{6,8}$ = 1.1 Hz; 1 H, H-8), 7.93 (dd, $J_{6,7}$ = 2.2 Hz, $J_{6,8}$ = 1.1 Hz; 1 H, H-6). **B** (in DMSO-$d_6$): 19.05 (q; $SCH_3$), 117.07 (d; C-7), 123.31 (d; C-8), 126.12 (s; C-8a), 137.54 (d; C-6), 139.60 (s; C-2,3), 175.37 (s; C-4a). **C**: 1080, 1550, 1625, 3320. **D**: 215 (3.83), 251 (3.91), 300 (sh, 3.63), 347 (3.84), 473 (4.41).

3 **A**(in $CDCl_3$-DMSO-$d_6$): 2.15 (s; 3 H, $CH_3$), 2.48 (s; 3 H, $CH_3$), 2.66 (s; 6 H, $SCH_3$), 6.38 (s; 1 H, H-8), 12.49 (s; 1 H, NH). **B** (in DMSO-$d_6$): 11.96 (q; $CH_3$), 15.11 (q; $CH_3$), 18.99 (q; $SCH_3$), 106.38 (d; C-8),

Table 2 (continued)

117.79 (s; C-8a), 133.88 (s; C-7), 138.66 (s; C-5), 142.96 (s; C-5), 181.07 (s; C-4a). **C**: 1080, 1510, 1600, 3270. **D**: 206 (4.09), 238 (3.98), 305 (4.01), 460 (4.37).

4 **A** (in DMSO-$d_6$): 2.77 (s; 6 H, $SCH_3$), 7.33-7.97 (m; 4 H, H-7,8,9,10), 8.95 (s; 1 H, H-5). **B** (in DMSO-$d_6$): 19.11 (q; $SCH_3$), 112.37 (s; C-10a), 114.55, 120.43, 125.37, 125.73 (4 d; C-7,8,9,10), 122.73 (s; C-10b), 137.85 (s; C-6a), 138.88 (s; C-2,3), 181.19 (s; C-4a). **C**: 1080, 1500,1625, 3250. **D**: 208 (4.40), 250 (4.04), 283 (4.06), 350 (3.50), 477 (4.37).

5 **A** (in $CDCl_3$): 2.50 (s; 6 H, $SCH_3$), 6.50 (d, J = 4 Hz; 1 H, H-7), 6.98 (d, J = 4 Hz; 1 H, H-8), 7.67 (s; 1 H, H-6). **B** (in $CDCl_3$): 19.08 (q; $SCH_3$), 124.12 (d; C-7), 124.37 (d; C-8), 131.21 (s; C-2,3), 141.42 (s; C-10b), 153.44 (d; C-6), 161.29 (s; C-4a). **C**: 1545. **D**: 232 (3.82), 298 (3.63), 340 (sh, 3.30), 446 (4.32).

6 **D**: 409 (4.08).

7 **A** (in $CDCl_3$): 2.54 (s; 6 H, $SCH_3$), 7.15-7.72 (m; 4 H, H-7,8,9,10), 8.12 (s; 1 H, H-5). **B** (in $CDCl_3$): 19.05 (q; $SCH_3$), 121.28 (s; C-10b), 120.46, 120.52, 124.52, 125.43 (4 d; C-7,8,9,10), 127.58 (s; C-10a), 130,12 (s; C-2,3), 152.26 (d; C-5), 154.17 (s; C-6a), 156.02 (s; C-4a). **C**: 1545. **D**: 211 (4.40), 254 (4.00), 270 (4.03), 310 (3.38), 442 (4.40).

9 **A** (in $CDCl_3$): 2.20 (s; 3 H, $C^3$-$CH_3$), 2.48 (s; 3 H, $C^1$-$CH_3$), 2.79 (s; 6 H, $SCH_3$), 6.10 (s; 1 H, H-4). **C** (in $CH_2Cl_2$): 1080, 1600, 1795, 3300. **D**: 207 (4.24), 248 (sh, 3.87), 326 (4.29).

10 **A** (in $CDCl_3$-DMSO-$d_6$): 3.05 (s; 6 H, $SCH_3$), 7.44 (mc; 4 H, benzo-H), 8.38 (d, J = 4 Hz; 1 H, H-3). **B** (in $CDCl_3$-DMSO-$d_6$): 18.51 (q; $SCH_3$), 96.23 (s; C-8b), 113.80, 118.07, 123.67, 124.49 (4 d; C-5,6,7,8), 125.55 (s; C-8a), 137.09 (s; C-4a), 140.42 (d; C-3), 151.57 (s; C-1,2). **C**: 1620, 1800, 3300. **D**: 213 (4.55), 250 (4.11), 275 (sh, 4.13), 286 (3.95), 342 (4.45).

12a **A** (in $CDCl_3$): 2.30 (s; 6 H, $C^{5,8}$-$SCH_3$), 2.50, 2.55 (2 s; 2 x 6 H, $C^{2,3,6,7}$-$SCH_3$). **B** (in $CDCl_3$): 19.36, 19.90, 20.51 (3 q; $SCH_3$), 127.03 (s; C-8a), 129.09 (s; C-5,8), 132.45 (s; C-2,3), 141.51 (s; C-6,7), 161.38 (s; C-4a). **C**: 1450, 1505, 2910. **D**: 208 (4.47), 270 (sh, 4.05), 335 (sh, 4.05), 490 (4.47).

12b **A** (in $CDCl_3$): 2.30 (s; 6 H, $C^{5,8}$-$SCH_3$), 2.48 (s; 6 H, $C^{6,7}$-$SCH_3$), 7.00 (s; 1 H, H-3), 7.43 (mc; 5 H, Ph). **B** (in $CDCl_3$): 20.14, 20.51 (2 q; $SCH_3$), 117.16 (d; C-3), 126.76 (d; Ph-C-m), 127.03 (s; Ph-C-i), 128.36 (s; C-8a), 129.18 (d; Ph-C-o), 129.36 (d; Ph-C-p), 131.21 (s; C-5,8), 140,84 (s; C-2), 141.03 (s; C-6,7), 164.35 (s; C-4a). **C**: 1455, 2920. **D**: 202 (4.64), 235 (4.45), 343 (3.46), 490 (4.53).

13 **A** (in $CDCl_3$): 2.35, 2.38 (2 s; 2 x 3 H, C(5,8)-$SCH_3$), 2.54, 2.56 (2 s; 2 x 3 H, C(6,7)-$SCH_3$), 7.36-7.78 (m; 5 H, Ph), 9.93 (s; H-4). **B** (in $CDCl_3$): 19.99, 20.38, 21.11, 21.46 (4 q; $SCH_3$), 124.85 (d; C-4), 126.60 (s; Ph-C-i), 127.24 (d; Ph-C-m), 129.39 (d; Ph-C-o), 130.09 (s; C-8a), 131.18 (d; Ph-C-p), 132.79 (s; C-5,8), 139.60, 140.10 (2 s; C-6,7), 164.83 (s; C-3), 167.83 (s; C-4a). **C**: 1475, 1490, 1525, 2920. **D**: 267 (3.93), 304 (sh, 3.42), 320 (sh, 3.82), 338 (4.00), 542 (4.37).

15a **A** (in $CDCl_3$): 1.58 (s; 3 H, C(5)-$SCH_3$), 2.36 (s; 3 H, C(7)-$SCH_3$), 2.56 (s; 6 H, C(2,3)-$SCH_3$), 2.88 (s; 3 H, C(8)-$SCH_3$), 3.11 (s; 3 H, C(6)-$SCH_3$), 5.18 (1 H, H-5). **B** (in $CDCl_3$-$CF_3CO_2H$): 9.81 (q; C(5)-S<u>C</u>$H_3$), 16.27 (q; C(8)-S<u>C</u>$H_3$), 17.51 (q; C(8)-S<u>C</u>$H_3$), 19.13 (q; C(6)-S<u>C</u>$H_3$),19.63 (q; C(2,3)-S<u>C</u>$H_3$), 54.85 (d; C-5), 130.85 (s; C-8a), 137.15 (s; C-7), 140.57 (s; C-2,3), 167.20 (s; C-8), 169.74 (s; C-6), 183.07 (s; C-4a). **C**: 1090, 1390. **D** (in $CH_3CN$-$HClO_4$ 9:1): 234 (4.19), 357 (3.77), 400 (3.80), 586 (4.33).

15b **A** (in $CF_3CO_2H$): 1.70 (s; 3 H, C(5)-$SCH_3$), 2.43 (s; 3 H, C(7)-$SCH_3$), 2.90 (s; 3 H, C(6)-$SCH_3$), 3.28 (s; 3 H, C(8)-$SCH_3$), 4.67 (s; 1 H, H-5), 7.52 (mc; 5 H, Ph), 7.87 (s; 1 H, H-3). **B** (in $CF_3CO_2H$):

Table 2 (continued)

9.84 (q; C(5)-S$\underline{C}H_3$), 16.27 (q; C(7)-S$\underline{C}H_3$), 17.54 (q; C(8)-S$\underline{C}H_3$), 19.17 (q; C(6)-S$\underline{C}H_3$), 55.34 (d; C-5), 122.82 (d; C-3), 127.85 (d; Ph-C-m), 129.24 (s; Ph-C-i), 130.73 (s; C-8a, Ph-C-o), 132.15 (d; Ph-C-p), 136.94, (s; C-7), 150.08 (s; C-2), 169.50 (s; C-8), 169.80 (s; C-6), 182.20 (s; C-4a). **D** (in $CH_3CN$-$HClO_4$ 9:1): 245 (4.41), 350 (4.01), 329 (4.02), 569 (4.59).[3]

16 **A** (in $CF_3CO_2H$): 1.70 (s; 3 H, C(5)-$SCH_3$), 2.45 (s; 3 H, C(7)-$SCH_3$), 2.88 (s; 3 H, C(6)-$SCH_3$), 3.05 (s; 3 H, C(8)-$SCH_3$), 4.93 (s; 1 H, H-5), 7.63 (mc; 5 H, Ph), 8.60 (s; 1 H, H-4). **B** (in $CF_3CO_2H$): 9.51 (q; C(5)-S$\underline{C}H_3$), 16.17 (q; C(7)-S$\underline{C}H_3$), 17.33 (q; C(8)-S$\underline{C}H_3$), 19.26 (q; C(6)-S$\underline{C}H_3$), 54.85 (d; C-5), 128.49 (d; Ph-C-m), 129.33 (d; C-4), 130.64 (d, s; Ph-C-i,o), 134.88 (d; Ph-C-p), 135.76 (s; C-4a), 136.42 (s; C-7), 166.29 (s; C-4), 171.71 (s; C-8), 175.46 (s; C-6), 180.30 (s; C-8a). **D** (in $CH_3CN$-$HClO_4$ 9:1): 250 (4.39), 274 (4.37), 375 (4.21), 400 (sh, 4.15), 585 (4.53).[3]

18 **A** (in $CDCl_3$): 1.43 (t, J = 7 Hz; 3 H, $SCH_2C\underline{H}_3$), 1.45 (t, J = 7 Hz; 3 H, $SCH_2C\underline{H}_3$), 3.18 (q, J = 7 Hz; 2 H, $S\underline{C}H_2CH_3$), 3.35 (q, J = 7 Hz; $S\underline{C}H_2CH_3$), 6.98 (s; 1 H, H-3), 7.36 (mc; 5 H, Ph). **C**: 1465, 1486, 1516, 1539, 1635. **D**: 220 (4.21), 338 (4.19), 376 (4.03), 535 (4.25).

## Conclusion

The reaction of pyrroles and indole with tris-methylthio-1,3-dithiolium tetrafluoroborate and tris-methylthio-cyclopropenylium tetrafluoroborate, respectively, gives rise to bis-methylthio-5-aza-1,4-dithiafulvalenes and bis-methylthio-2-azacalicenes which are candidates for the preparation of charge transfer complexes and radical cation salts. A related group of electron-rich alkylthio-substituted (aza)dithiafulvalenes is formed when sodium pentakis-methylthio-cyclopentadienide and tris-ethylthio-imidazole are reacted with 3-methylthio-1,2-dithiolium or 2-methylthio-1,3-dithiolium salts. Of particular interest among the compounds obtained through this novel condensation is hexakis-methylthio-1,4-dithiafulvalene.

## Experimental

$^1H$ NMR spectra were determined on Varian EM 360 and Bruker WP 80 spectrometers, $^{13}C$ NMR spectra on a Bruker WP 80 spectrometer (TMS as internal standard). IR spectra were determined on Perkin-Elmer 125 and 157 spectrophotometers. UV/VIS spectra were determined on a Zeiss DMR 10 spectrometer. Melting points were determined on a Büchi SMP-20 apparatus and are uncorrected.

General procedure for the preparation of azadithiafulvalene salts 2-4 and azadithiafulvalenes 5-7. 2/5: To a hot solution of 0.65 g (2 mmol) 1 (ref. 32,39) in 10 ml acetonitrile was added 0.13 g (2 mmol) pyrrole whereupon the solution turned deep red. After 4 h at room temperature the precipitate 2 was isolated by filtration and recrystallized from acetonitrile. To a suspension of 2.9 g (8.38 mmol) pulverized 2 in 10 ml dry acetonitrile was added at -40°C 1.2 g (9.22 mmol) ethyldiisopropylamine and the mixture warmed slowly to room temperature. After 4 h the brown precipitate 5 was isolated by filtration, washed with acetonitrile and recrystallized from acetonitrile.

Tris-methylthio-cyclopropenylium-tetrafluoroborate (8): To a solution of 1.78 g (10 mmol) tetrachlorocyclopropene in 50 ml dry methylene chloride was added dropwise 2.8 g (30 mmol) dimethyl disulfide, followed by 1.96 g dimethylmethylthiosulfoniumtetrafluoroborate (ref. 28). After stirring the mixture 5 d at room temperature, diethyl ether was added to the solution and the precipitate filtered off. Yield 1.98 g (75%), m.p. 151-153°C (dec.), ref. 25: dec. > 130°C.

General procedure for the preparation of azacalicenes 9,10: To a solution of 0.36 g (3.79 mmol) 2,5-dimethylpyrrole in 3 ml acetonitrile was added 1.0 g (3.79 mmol) 8 and the mixture heated under reflux for 1 h. After cooling to 20°C, 10 crystallized in pure form. 9 was obtained after ethyl acetate was added to the mixture, and recrystallized from acetonitrile/ethyl acetate.

General procedure for the preparation of poly-ethylthio-dithiafulvalenes 12,13: 2.5 g (7.64 mmol) 1 (or 1.6 g (5 mmol) 2-methylthio-4-phenyl-1,3-dithiolium-perchlorate or 1.6 g 3-methylthio-5-phenyl-1,2-dithiolium-perchlorate) was added to a solution of 2.43 g (7.64 mmol) 11b (or 1.6 g (5 mmol)) in 30 ml dry acetonitrile. The deep red solution was stirred for 24 h at 20°C, the precipitate then isolated by filtration and recrystallized from acetonitrile.

4,5-Bis-methylthio-2-(2,3,4,5-tetrakis-methylthio-1,3-cyclopentadien-1-yl)-1,3-dithiolium-perchlorate (15a): To a solution of 0.22 g (0.52 mmol) 12a in 5 ml acetonitrile was added 0.10 g (0.67 mmol) 70% perchloric acid. The mixture turned deep red immediately. After 1 h, the precipitate was isolated by filtration and recrystallized from a small amount of acetonitrile.

General procedure for the preparation of 5,7-diazadithiafulvalenes 18,19. 18: To a suspension of 0.28 g (1 mmol) 17 (ref. 40) and 0.32 g (1 mmol) 2-methylthio-4-phenyl-1,3-dithiolium-perchlorate (or 3-methylthio-5-phenyl-1,2-dithiolium-perchlorate) in 5 ml dry acetonitrile was added 0.26 g (2 mmol) ethyldiisopropylamine, the mixture stirred for 30 min at room temperature and then kept in a refrigerator for 2 d. The precipitate was isolated by filtration and recrystallized from acetonitrile.

**Table 3** Yields, melting points and elemental analyses of 2-5,7-10,12,13,15a,16,18,19

| | | yield<br>m.p.<br>(°C) | molecular formula<br>elemental analysis, C H N<br>calcd/found |
|---|---|---|---|
| 2 | 2-(2-Pyrrolyl)-4,5-bis-methylthio-1,3-dithiolium-tetrafluoroborate<br>[bluish-shining prisms] | 0.63 g<br>(91%)<br>186-188 | $C_9H_{10}BF_4NS_4$ (347.2)<br>31.13 2.90 4.03/31.45 3.01 3.93 |
| 3 | 2-(2,5-Dimethyl-3-pyrrolyl)-4,5-bis-methylthio-1,3-dithiolium-tetrafluoroborate<br>[dark-red needles] | 0.74 g<br>(99%)<br>256-257 | $C_{11}H_{14}BF_4NS_4$ (375.3)<br>35.21 3.76 3.73/34.85 3.82 3.56 |
| 4 | 2-(3-Indolyl)-4,5-bis-methylthio-1,3-dithiolium-tetrafluoroborate<br>[dark-red needles] | 2.95 g<br>(87%)<br>232-234 | $C_{13}H_{12}BF_4NS_4$ (397.3)<br>39.30 3.04 3.52/39.13 3.02 3.45 |
| 5 | 2-(4,5-Bis-methylthio-1,3-dithiol-2-yliden)-2H-pyrrole<br>[brown needles] | 1.7 g<br>(81%)<br>75-77 | $C_9H_9NS_4$ (259.4)<br>41.67 3.50 5.40/41.80 3.49 5.54<br>S 49.43/49.34 |
| 7 | 3-(4,5-Bis-methylthio-1,3-dithiol-2-yliden)-3H-indole<br>[red needles] | 0.60 g<br>(97%)<br>128 | $C_{13}H_{11}NS_4$ (309.5)<br>50.45 3.58 4.53/50.49 3.57 4.62<br>S 41.44/41.42 |
| 9 | 2,5-Dimethyl-3-pyrrolyl-bis-methylthio-cyclopropenylium-tetrafluoroborate | 0.9 g<br>(76%)<br>198-199 | $C_{11}H_{14}BF_4NS_2$ (311.2)<br>42.46 4.53 4.50/42.90 4.78 4.20 |
| 10 | Indol-3-yl-bis-methylthio-cyclopropenylium-tetrafluoroborate<br>[pink-beige crystals] | 0.28 g<br>(56%)<br>245-246 | $C_{13}H_{12}BF_4NS_2$ (333.2)<br>46.87 3.63 4.20/47.11 3.64 4.25 |
| 12a | 2-(Tetrakis-methylthio-2,4-cyclopentadien-1-yliden)-4,5-bis-methylthio-1,3-dithiole<br>[red platelets] | 1.2 g<br>(37%)<br>100 | $C_{14}H_{18}S_8$ (442.8)<br>37.98 4.10/38.28 4.05<br>S 57.93/57.93 |
| 12b | 2-(Tetrakis-methylthio-2,4-cyclopentadien-1-yliden)-4-phenyl-1,3-dithiole<br>[dark-green shining platelets] | 1.3 g<br>(62%)<br>144 | $C_{18}H_{18}S_6$ (426.7)<br>50.67 4.25/50.93 4.23<br>S 45.08/45.00 |
| 13 | 3-(Tetrakis-methylthio-2,4-cyclopentadien-1-yliden)-5-phenyl-1,2-dithiole<br>[black-golden shining needles] | 0.9 g<br>(37%)<br>110 | $C_{18}H_{18}S_6$ (426.7)<br>50.67 4.25/50.93 4.39<br>S 45.08/45.21 |
| 15a | 4,5-Bis-methylthio-2-(2,3,4,5-tetrakis-methylthio-1,3-cyclopentadien-1-yl)-1,3-dithiolium-perchlorate<br>[bluish-black shining needles] | 0.17 g<br>(62%)<br>130<br>(dec.) | $C_{14}H_{19}ClO_4S_8$ (543.2)<br>30.95 3.53/30.93 3.62 |
| 18 | 2,5-Bis-ethylthio-4-(4-phenyl-1,3-dithiol-2-yliden)-4H-imidazole<br>[green shining needles] | 0.20 g<br>(55%)<br>137-138 | $C_{16}H_{16}N_2S_4$ (364.6)<br>52.71 4.42 7.68/52.82 4.40 7.51<br>S 35.18/35.34 |
| 19 | 2,5-Bis-ethylthio-4-(5-phenyl-1,2-dithiol-3-yliden)-4H-imidazole<br>[violet needles] | 0.40 g<br>(55%)<br>117-118 | $C_{16}H_{16}N_2S_4$ (364.6)<br>52.71 4.42 7.68/53.23 4.59 7.39 |

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