A NOVEL APPROACH TO *N, N'*-DIMETHYL AND *N, N'*-ETHYLENE BRIDGED DIBENZODITHIADIAZAFULVALENE

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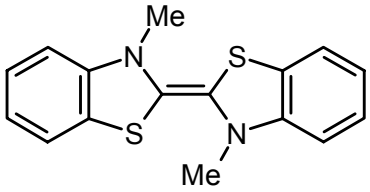
Abstract

A novel approach to electron rich olefins such as dibenzodithiadiazafulvalenes (DTDAFs) is reported. These compounds have been prepared by alkylation of the benzothiazole-2-thione ring. The first crystal structure of the *N,N'*-dimethyl dibenzoDTDAF dication is also reported.

Introduction

Electron rich olefins such as tetrachalcogenafulvalenes have been widely used as constituents of organic materials.[1] Contrariwise, only a few examples of dithiadiazafulvalenes (DTDAF) have been studied in this research area,[2-5] even if they are known for almost 40 years.[6] This is probably due to the fact that DTDAF are highly oxygen-sensitive and therefore difficult to handle for the preparation of charge transfer salts. For example, on exposure to air, oxidative rearrangement of *N,N'*-dimethyl dibenzoDTDAF **1** has been observed.[7] Surprisingly, *N,N'*-dimethyl dibenzoDTDAF was, for a long time, the only representative of its family which was employed in the charge transfer salts.[8] Nevertheless, until now no crystal structure of either the neutral *N, N'*-dimethyl dibenzoDTDAF or its salts have been described. This DTDAF was prepared by intermolecular basic coupling of the corresponding *N*-methyl benzothiazolium salt.[6] Using dibenzothiazole, Hünig et al. prepared also the *N, N'*-ethylene bridged dibenzoDTDAF.[9] In this article, we report a novel approach for the synthesis of either *N,N'*-dimethyl or *N, N'*-ethylene bridged dibenzo-DTDAF starting from benzothiazole-2-thione. Our strategy allowed us to analyse the electron donating

properties of the donors and to trap one of these derivatives with oxydizing agent in order to form a dication salt. In addition we report the first crystal structure of the dication salt of *N,N'*-dimethyl dibenzo-DTDAF.



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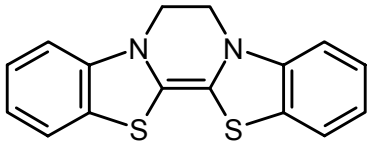

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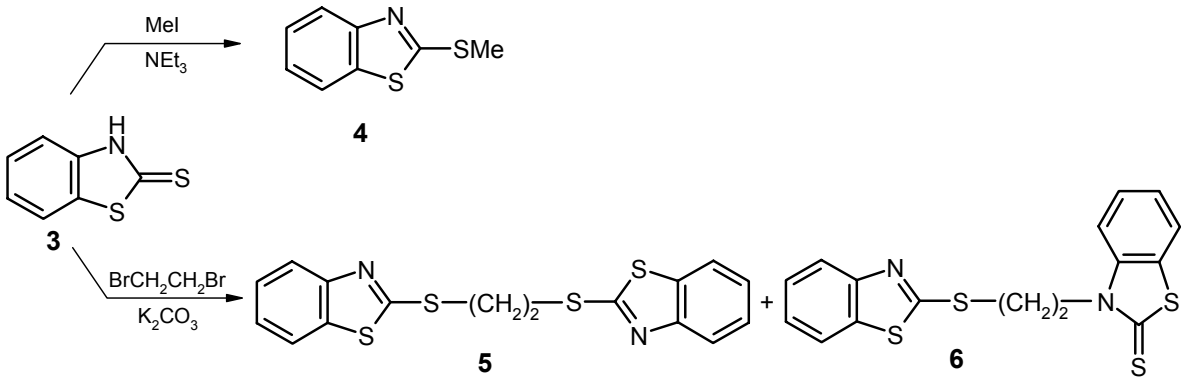
Results and discussion

Our approach consists in the use of benzothiazole-2-thione **3** as the versatile precursor of the DTDAF framework. Alkylation of **3** in the presence of triethylamine with alkyl halides such as methyl iodide proceeds exclusively on the exocyclic sulfur atom and 2-methylthio benzothiazole **4** was isolated in good yields (Scheme 1).[10] In order to create a bridge between the two thiazole cores, we used dibromoethane as the alkylating agent. In the case of bishalogenated alkanes, the overall reaction with **3** is more complex.

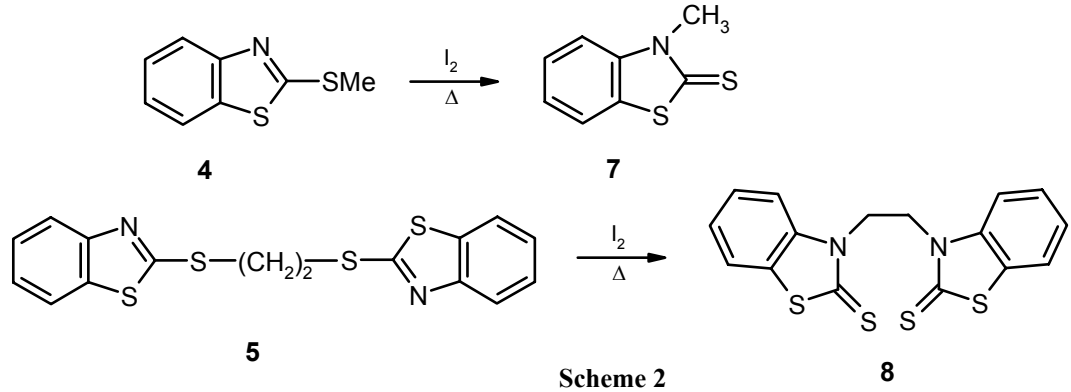


4 **3** **5** **6**

Scheme 1

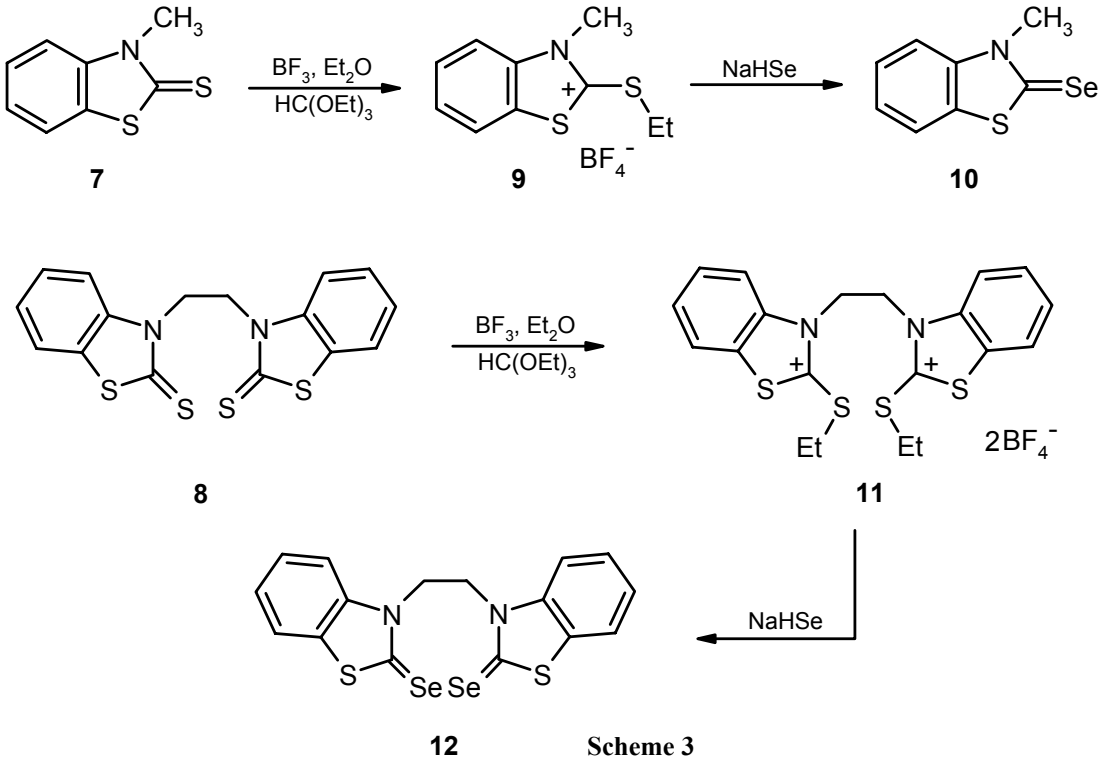
For instance, Stanovnik and Tišler observed *S, S*-intermolecular alkylation and *S, N*-intramolecular alkylation giving bicyclic systems, using one equivalent of dibromoethane.[11] In our case, addition of half equivalent of 1,2-dibromoethane to benzothiazole-2-thione **3** in the presence of potassium carbonate at a higher temperature afforded the product **5** resulting from *S, S*-intermolecular alkylation in 70% yield together with a minor amount of the *N, S*-intermolecular bisalkylated derivative **6** (12%). Sexton et al. found that *S*-alkyl benzothiazole derivatives undergo thermal

rearrangement to their *N*-alkyl isomers in the presence of iodine without the use of solvent.[12]



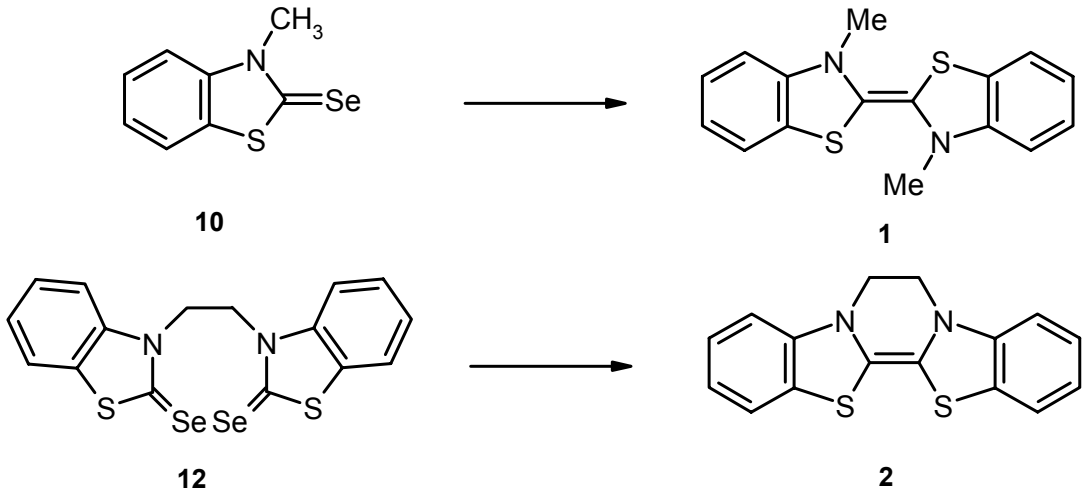
Scheme 2

Therefore the key step of our novel approach to *N,N'*-dimethyl and *N,N'*-ethylene bridged dibenzo DTDAF is the use of this thermal isomerisation as already described for **4**[13] and later for **5**[13] but the *N, N'*-isomer was isolated in 28% yield and poorly characterized. We performed thermal treatment of **4** in the presence of iodine at temperatures between 200 and 220 °C for 8 hours and *N*-methyl benzothiazole-2-thione **7** was isolated in good yields (74%). We applied the same strategy to 2,2'-ethylenebisthiobenzothiazole **5** at a temperature range of 220-250 °C and using this modified work up, we isolated **8** in 41% yield (Scheme 2).



Scheme 3

In order to form the dithiadiazafulvalenes **1** and **2**, we converted the thiazoline-thione **7** and **8** into the corresponding thiazoline-2-selone **10** and **12**. Alkylation of the exocyclic sulfur with diethoxycarbonium tetrafluoroborate,[14] formed in situ from $BF_3.Et_2O$ and triethyl orthoformate yielded the corresponding salts **9** and **11**. Then treatment of these salts with sodium hydrogen selenide lead to benzothiazole-2-selone **10** and dibenzothiazole-2-selone **12** in excellent yields (Scheme 3). The coupling of benzothiazole-2-selone **10** and dibenzothiazole-2-selone **12** in the presence of triethylphosphite in refluxing toluene under inert atmosphere, afforded either *N, N'*-dimethyl dibenzo-DTDAF (**1**) or *N,N'*-ethylene bridged dibenzoDTDAF (**2**). Those donors are difficult to isolate without further oxidation with oxygen, thus formation of either a spiroamide derivative or a macrocycle dithiadiazecine-dione is often obtained after air exposure.[7]



Scheme 4

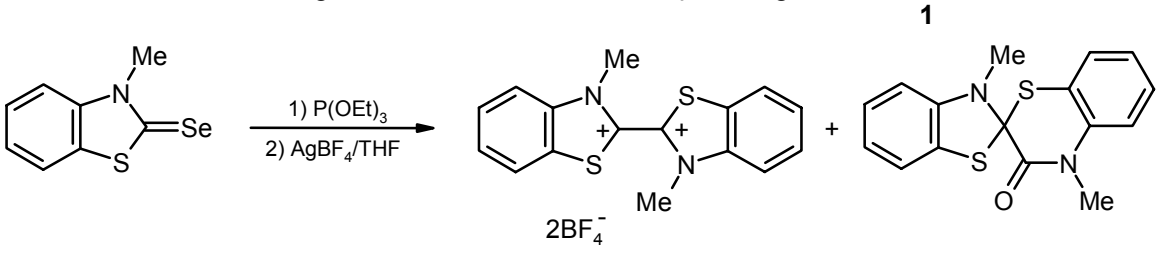
Therefore, in order to get information on their redox properties we realized electrochemical investigations directly on the medium where the donor was formed by adding the reaction mixture, under inert atmosphere, to a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2. The oxidation potentials of dibenzo-DTDAFs obtained by cyclic voltammetry are listed in Table 1 together with the redox potentials of the dibenzo-DTDAFs prepared by Hünig et al.[15] In both cases, two main reversible oxidation waves, associated with the redox behavior of the donors, were observed at low potentials corresponding respectively to the formation of the radical cation and dication of the dithiadiazafulvalene. As can be seen in Table 1 similar

oxidation potentials were previously obtained for both donors using another synthetic approach.[9]

Table 1 Oxidation potentials in V *vs* SCE of donors **1** and **2**

	Epa^1/ V	Epa^2/ V	□E mV
DTDAF **1**	-0.15	+0.05	200
DTDAF **1** [15]	-0.17	-0.02	150
DTDAF **2**	-0.21	+0.33	540
DTDAF **2** [15]	-0.23	+0.26	490

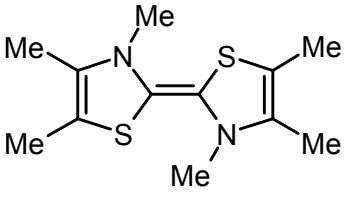
Pt working electrode with 0.1 M n-Bu_4NPF_6 scanning rate 0.1V/s



10 **13** **14**

Scheme 4

We chemically oxidized the *N,N'*dimethyl dibenzo DTDAF *in situ* in order to form the dication which should be easier to handle. Immediately after the addition of $AgBF_4$ solution, abundant black precipitate of Ag^0 was observed in the medium, which indicated that donor **1** was oxidized. A mixture of the dication **13** and the spiroamide **14**[7] was obtained as suggested by ^{1}H NMR spectra of crude product (Scheme 5).



15

Recrystallization of the dication **13** from HCOOH/MeCOOH afforded crystals suitable for X-ray diffraction. An interesting feature concerns the geometry of dication, where we observed that both heterocyclic cores are planar and located in planes almost perpendicular to each other (Figure 1). So far no crystal structure of the neutral or

oxidized *N,N'*-dimethyl dibenzo DTDAF has been described in the literature. However, in comparison with hexamethylDTDAF **15**[16] we can reasonably postulate that the neutral donor **1** would be almost planar and the structure obtained for the dication **13** indicates that important conformational modification occurred during the oxidation, which minimized columbic repulsion between positively charged heterocyclic cores.

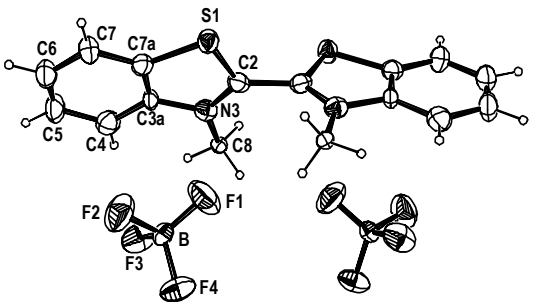


Figure 1 : X-Ray molecular structure of dication **13** showing the numbering of atoms

This twist structure of the dication was also observed for **15**.[2-5] Furthermore, this conformational modification upon oxidation gives an insight into the small potential difference observed between the two-oxidation states ($\Delta E = Epa_2 - Epa_1$) for *N,N'*-dimethyl dibenzoDTDAF **1** (Table 1). Contrariwise, the *N,N'*-bridge prevents conformational modifications upon oxidation and therefore the ΔE is larger for *N,N'*-ethylene dibenzo-DTDAF **2**.

Conclusions

In summary we have developed a novel approach to either *N,N'*-dimethyl or *N,N'*-ethylene dibenzo-DTDAF, both excellent electron rich olefins, *via* alkylation of benzothiazole 2-thione. The key to this strategy involves the thermal rearrangement of *S*-alkyl benzothiazole derivatives into the *N*-alkylbenthiazole one. Chemical oxidation of the *N,N'*-dimethyl dibenzoDTDAF allowed us to isolate the corresponding dication and for the first time a crystal structure of this derivative is presented. It would be of interest to study other bis alkylating agent in the first step of our synthetic approach in order to modulate the length of the *N,N'*-bridge, *via* the thermal isomerisation, and therefore tune the redox properties of the donor.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$, unless otherwise indicated, at 200 and 300 MHz and ^{13}C NMR spectra at 50 and 75 MHz. Chemical shifts are reported in ppm referenced to TMS. Melting points were measured using a Kofler hot stage apparatus. Elemental analyses were obtained from the Laboratoire Central de Microanalyse du CNRS (Lyon) and from Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia. Column chromatography was performed on silica gel 60 (0.040-0.063 mm). CH_2Cl_2 and CH_3CN were dried by refluxing over P_2O_5 followed by distillation and toluene was dried by refluxing over NaH followed by distillation.

2-Methylthio-benzoazole (4). To a suspension of 3*H*-benzothiazole-2-thione **3** (15.00 g, 89.68 mmol) in CH_2Cl_2 (100 mL), a solution of iodomethane (19.09 g, 134.52 mmol) in CH_2Cl_2 (30 mL) and triethylamine (13.61 g, 134.52 mmol) in CH_2Cl_2 (30 mL) were respectively added. The exothermic reaction took place immediately giving orange solution. The reaction mixture was stirred at room temperature for 10 min and was then extracted with water (5×30 mL). The organic phase was dried over Na_2SO_4. Evaporation of the solvent afforded dark orange oil that solidified which was distilled two times (Kugelrohr, 0.04 mbar, 115 °C) to give **4**. The white crystalline solid **4** (14.60 g, 90%), melted at 43 °C (lit.[10] 48-49 °C). *Anal*. Calculated for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.73. Found: C, 52.93; H, 3.95; N, 7.77. ^{1}H NMR ($CDCl_3$): δ 7.81-7.66 (1H, dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz), 7.62-7.49 (1H, dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz), 7.32-7.18 (1H, td, J_1 = 8.1 Hz, J_2 = 1.3 Hz), 7.17-7.01 (1H, td, J_1 = 7.8 Hz, J_2 = 1.3 Hz), 2.59 (3H, s). ^{13}C NMR ($CDCl_3$): δ 168.47, 153.80, 135.59, 126.48, 124.51, 121.80, 121.40, 16.36.

2,2'-Ethylenedithiobis(benzothiazole) (5). 3*H*-Benzothiazole-2-thione (**3**, 15.00 g, 89.68 mmol) and K_2CO_3 (12.40 g, 89.68 mmol) were suspended in EtOH (50 mL). The suspension was heated to reflux and 1,2-dibromoethane (8.43 g, 44.84 mmol), dissolved in 10 mL of EtOH, was added. The reaction mixture was vigorously stirred at reflux for 30 min. After cooling of the mixture at room temperature, the precipitate was filtered and dried. A suspension of this precipitate in CH_2Cl_2 (250 mL) was stirred at room temperature for 1 h and undissolved inorganic salts were filtered off. The filtrate was evaporated under reduced pressure and 60 mL of acetone were added to the residue. The

mixture was heated to boiling. The hot suspension was filtered and after drying **5** was obtained as white crystalline powder. Filtrate was evaporated and the brown residue was chromatographied over silica gel (CH_2Cl_2/petroleum ether : 1/1) to afford remained quantity of **5** and **6** as the major side product of the reaction.

The product **5** (11.24 g, 70%), melted at 148.5 °C (lit.[11] mp 150°C). *Anal.* Calculated for $C_{16}H_{12}N_2S_4$: C, 53.30; H, 3.35; N, 7.77. Found: C, 53.55; H, 3.30; N, 7.77. ^{1}H NMR: δ 7.97-7.76 (4H, m), 7.55-7.28 (4H, m), 3.89 (4H, s). ^{13}C NMR: δ 165.93, 153.56, 135.84, 126.51, 124.82, 122.07, 121.46, 33.39.

The product **6** white needles (1.95 g, 12%), melted at 151.5 °C. *Anal.* Calculated for $C_{16}H_{12}N_2S_4$: C, 53.30; H, 3.35; N, 7.77. Found: C, 53.24; H, 3.32; N, 7.80. ^{1}H NMR: δ 7.98-7.84 (2H, m), 7.81-7.69 (1H, d, J = 7.83 Hz), 7.52-7.38 (3H, m), 7.36-7.21 (2H, m), 4.84 (2H, m), 3.67 (2H, m). ^{13}C NMR: δ 189.68, 166.24, 153.25, 142.10, 135.94, 127.99, 127.45, 126.67, 125.34, 125.04, 121.76, 121.74, 121.65, 113.77, 45.80, 29.00.

3-Methyl-3*H*-benzothiazole-2-thione (7). A 25 mL round bottom flask containing 2-methylthio-benzoazole **4** (4.90 g, 27.03 mmol) and iodine (0.28 g) was placed in a metallic bath. The temperature of the bath was maintained between 206 and 220 °C while the reaction mixture was stirred for 8 hours. Upon cooling to the room temperature reaction mixture solidified and a brown solid was obtained. The solid was dissolved in CH_2Cl_2 and the dark brown solution was extracted with an aqueous 5% Na_2SO_3 solution (30 mL) in order to remove residual iodine. The organic layer was dried over Na_2SO_4 and evaporated. The residue was flash chromatographed over silica gel (CH_2Cl_2). Evaporation of the solvent afforded yellow oil, which soon solidified and furnished crude product (4.80 g, 98%) as a yellow solid. The product **7** (3.63 g, 74%) yellow needles, melted after recrystallization from EtOH at 85 °C (lit.[10] 90-91 °C). *Anal.* Calculated for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.73. Found: C, 53.02; H, 3.98; N, 7.78. ^{1}H NMR ($CDCl_3$): δ 7.79-7.34 (4H, m), 4.04 (3H, s). ^{13}C NMR ($CDCl_3$): δ 189.75, 142.41, 127.91, 127.46, 125.30, 121.70, 112.79, 33.60.

3,3'-Ethylenebis(benzothiazole-2-thione) (8). A 50 mL round bottom flask containing 2,2'-ethyelenedithiobis(benzothiazole) **5** (7.25 g, 20.10 mmol) and iodine (0.40 g) was

placed in a metallic bath with a starting temperature of 212 °C. The reaction mixture was stirred for 1 h while temperature of the bath was maintained between 212 and 221 °C. Then, the temperature of the bath was raised and the mixture was stirred further for 2 h while temperature of the bath was kept between 220 and 250 °C. Upon cooling to room temperature the reaction mixture solidified which was partially solubilized in CH_2Cl_2 (300 mL). The insoluble dark brown crystalline solid was filtered off and the filtrate was extracted with 5% Na_2SO_3 solution (30 mL) in order to remove residual iodine. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue and the dark brown crystalline solid were flash chromatographed over silica gel using CH_2Cl_2 as eluent to afford an orange-brown powder. After recrystallization from 60 mL of pyridine a yellow crystalline precipitate was obtained. Filtration afforded **8** as yellow needles. Remained quantity of **8** were obtained from the filtrate after evaporation of the solvent, flash chromatography over silica gel (CH_2Cl_2) and recrystallization in 10 mL of pyridine. The product **8**, (3.00 g, 41%), melted after recrystallization at 276.5 °C (dec) (lit.[13] mp 226-268 °C). *Anal.* Calculated for $C_{16}H_{12}N_2S_4$: C, 53.30; H, 3.35; N, 7.77. Found: C, 53.06; H, 3.38; N, 7.89. ^{1}H NMR: δ 7.64-7.49 (2H, d, J = 8.07 Hz), 7.44-7.10 (6H, m), 4.83 (4H, s). ^{13}C NMR: δ 190.18, 141.84, 127.95, 127.59, 125.46, 121.62, 112.83, 42.49.

2-Ethylthio-3-methyl-benzothiazolium tetrafluoroborate (9). To a stirred solution of 3-methyl-3*H*-benzoazole-2-thione **7** (1.50 g, 8.27 mmol) in $CHCl_3$ (30 mL) were added $CH(OEt)_3$ (4.91 g, 33.10 mmol) in $CHCl_3$ (10 mL) and $BF_3{\cdot}Et_2O$ (6.25 g, 44.10 mmol) in $CHCl_3$ (10 mL). The mixture was stirred at reflux for 1 hour. The reaction mixture was allowed to reach room temperature and approximately 3/4 of the solvent were removed under reduced pressure. Diethyl ether was added to the resulting solution. The light brown solid that precipitated was filtered off, washed with ether and dried to give **9**. The product **9** (2.24 g, 91%) melted at 141 °C. *Anal.* Calculated for $C_{10}H_{12}NS_2BF_4$: C, 40.42; H, 4.07; N, 4.71. Found: C, 40.17; H, 4.12; N, 4.84. ^{1}H NMR (CD_3CN): δ 8.42-8.32 (1H, dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz), 8.22-8.12 (1H, dd, J_1 = 7.8 Hz, J_2 = 0.8 Hz), 8.09-7.98 (1H, m), 7.97-7.85 (1H, m), 4.23 (3H, s), 3.77 (2H, q, J = 7.3 Hz), 1.80 (3H, t, J = 7.3 Hz). ^{13}C NMR (CD_3CN): δ 179.84, 142.17, 129.22, 128.00, 127.23, 123.14, 115.12, 36.19, 30.82, 12.32.

3-Methyl-3*H*-benzothiazole-2-selone (10). A stream of nitrogen was bubbled for 15 min through a stirred solution of $NaBH_4$ (0.62 g, 16.29 mmol) in absolute EtOH (110 mL for). Then, black selenium powder (1.17 g, 14.81 mmol) was added into a solution under a flux of nitrogen. The mixture was stirred under nitrogen at room temperature until the formation of the turbid colorless solution of NaHSe. A solution of 2-ethylthio-3-methyl-benzoazolium tetrafluoroborate **9** (2.20 g, 7.40 mmol) in MeCN (25 mL) was slowly injected into a solution of NaHSe. The reaction mixture was stirred under nitrogen at room temperature for 30 min. Water (100 mL) was added and the mixture was extracted with CH_2Cl_2 (5 ×50 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave orange crystalline solid, which was contaminated with some red selenium. The solid was flash chromatographied over silica gel (CH_2Cl_2) two times in order to eliminate residual red selenium. Product containing fractions were collected and combined. Evaporation of the solvent under reduced pressure furnished **10** (1.65 g, 98%), yellow crystals, mp 110 °C. *Anal.* Calcd for C_8H_7NSSe: C, 42.11; H, 3.09; N, 6.14. Found: C, 42.25; H, 3.19; N, 6.24.^{1}H NMR ($CDCl_3$): δ 7.70-7.37 (4H, m), 4.05 (3H, s). ^{13}C NMR ($CDCl_3$): δ 185.53, 143.47, 130.81, 127.71, 125.67, 121.63, 113.37, 36.08.

3,3'-Ethylenebis(2-ethylthiobenzothiazolium tetrafluoroborate) (11). To a suspension of 3,3'-ethylenebis(benzoazole-2-thione) **8** (1.00 g, 2.77 mmol) in toluene (50 mL), solutions of $CH(OEt)_3$ (3.30 g, 22.19 mmol in 5 mL of toluene) and $BF_3{\cdot}Et_2O$ (4.20 g, 29.56 mmol in 5 mL of toluene) were added. The reaction mixture was heated to reflux for 2 hours and then cooled to room temperature. Ether (30 mL) was added, the precipitate was filtered off, washed with ether and dried to give **11** as a pale brown powder. The product **11** (1.62 g, 99%),melted at 234 °C (dec). *Anal.* Calculated for $C_{20}H_{22}N_2S_4B_2F_8$: C, 40.56; H, 3.74; N, 4.73. Found: C, 40.25; H, 3.83; N, 4.73.^{1}H NMR (DMSO-d_6): δ 8.61-8.43 (2H, d, J = 7.06 Hz), 8.28-8.10 (2H, d, J = 8.07 Hz), 8.04-7.80 (4H, m), 5.32 (4H, s), 3.64 (4H, q, J = 7.25 Hz), 1.44 (6H, t, J = 7.28 Hz). ^{13}C NMR (DMSO-d_6): δ 182.16, 141.76, 130.13, 128.63, 128.15, 124.92, 115.35, 47.32, 31.51, 13.29.

3,3'-Ethylenebis(benzothiazole-2-selone) (12). $NaBH_4$ (113 mg, 2.97 mmol), was dissolved in absolute EtOH (30 mL) and a stream of nitrogen was bubbled for 15 min into the solution. Selenium powder (213 mg, 2.70 mmol) was added into the solution under a flux of nitrogen. Then the mixture was stirred at room temperature for 15 min. Then **11** (400 mg, 0.68 mmol), dissolved in MeCN (20 mL), was slowly added. The reaction mixture was stirred at room temperature under nitrogen for 40 min. Water (50 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3□100 mL). Combined organic layers were evaporated under reduced pressure. The orange-yellow residue was dissolved in hot pyridine (20 mL) in order to eliminate red selenium by filtration. Evaporation of pyridine gave **12** as a green-yellow powder. The product **12** (0.25 g, 81%) melted after recrystalization in pyridine at 291 °C (dec). *Anal.* Calculated for $C_{16}H_{12}N_2S_2Se_2$: C, 42.30; H, 2.66; N, 6.17. Found: C, 42.64; H, 2.65; N, 6.49. ^{1}H NMR: δ 8.01-7.86 (2H, d, J = 8.07 Hz), 7.54-7.40 (4H, m), 7.37-7.26 (2H, m), 5.12 (4H, s). ^{13}C NMR: δ 185.93, 143.04, 130.33, 128.14, 125.80, 121.40, 113.68, 44.95.

***N,N'*-dimethyldibenzoDTDAF (1).** A solution of 3-methylbenzoazole-2-selone **10** (20.0 mg, 0.088 mmol) in freshly distilled toluene (2 mL) was heated to reflux under nitrogen and freshly distilled triethylphosphite (24 μL, 0.14 mmol) was added dropwise. The reaction mixture was stirred at reflux for 30 min giving an orange clear solution. The reaction mixture was cooled down to the room temperature and the solution was then transferred into an electrochemical cell under nitrogen to a degassed solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2. The CV of the solution was recorded after the addition of aluminum oxide (activated, basic, 150 mesh).

***N,N'*-Ethylene-bisbenzoDTDAF (2).** Same procedure as the one decribed above for the synthesis of **1** using 3,3'-ethylenebis(benzoazole-2-selone) **12** (20.0 mg, 0.044 mmol) in freshly distilled toluene (3 mL) and triethylphosphite (54.8 μL, 0.32 mmol).

2,2'-Bis(3-methyl-benzothiazolium tetrafluoroborate) (13). Same procedure as above for the preparation of **1** using 3-methylbenzoazole-2-selone **10** (0.50 g, 2.19 mmol) in distilled toluene (12 mL) and triethylphosphite (1.40 mL, 8.18 mmol). After the reflux a

degassed solution of $AgBF_4$ (0.84 g, 4.33 mmol) in THF (30 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 1 hour and after left to stand under nitrogen over night. Et_2O (60 mL) was added and the precipitate was filtered, washed with Et_2O and dried to afford black powder. The powder was then suspended in MeCN (100 mL) and filtered three times trough Celite 521 to give clear yellow solution. The solution was evaporated to afford yellow crystalline solid (0.50 g). The solid was recrystallized from 12.5 mL of MeCOOH/HCOOH (1:1 v/v). The product **13** (200 mg, 39%), obtained as yellow crystals, melted at 250-258 °C (dec). *Anal.* Calculated for $C_{16}H_{14}N_2S_2B_2F_8$: C, 40.71; H, 2.99; N, 5.93. Found: C, 40.48; H, 3.06; N, 6.05. ^{1}H NMR (CD_3CN): δ 8.63-8.52 (2H, d, dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz), 8.50-8.37 (2H, dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz), 8.28-8.03 (4H, m), 4.37 (6H, s). ^{13}C NMR (CD_3CN): δ 153.33, 142.37, 133.43, 132.02, 131.08, 124.45, 118.04, 39.46.

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Povzetek

Opisali smo nov pristop do dibenzoditiadiazafulvalenov (DTDAFs), olefinov, bogatih na elektronih. Te spojine smo pripravili z alkiliranjem benzotiazol-2-tionovega obroča. Narejena je tudi prva kristalna struktura *N,N'*-dimetil dibenzoDTDAF dikationa.