Synthesis of Bis(ethylenedithio)dithiadiazafulvalenes (BEDT-DTDAF) and Generation of Charge-Transfer Complexes with Tetracyanoquinodimethane

Sławomir Makowiec,* Wioletta Koczan, Janusz Rachoń

Department of Organic Chemistry, Faculty of Chemistry, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland
Fax +48(58)3472694; E-mail: mak@chem.pg.gda.pl

Received 25 October 2007; revised 15 November 2007

Abstract: The synthesis of bis(ethylenedithio)dithiadiazafulvalenes (BEDT-DTDAFs), in four steps via 4,5-(ethylenedithio)thiazole and 3-alkyl-4,5-(ethylenedithio)thiazolium salts, and the generation of conducting charge-transfer complexes from a new type of dithiadiazafulvalene and tetracyanoquinodimethane are reported.

Key words: carbenes, complexes, heterocycles, organic metals, fulvalenes

Tetraheterafulvalenes, such as TTF, TSeF, TTeF, and DTDAF, are widely used for the preparation of organic metals and organic superconductors.[1–8] So far, many modified variants to the four parent compounds have been synthesized. One of the most noteworthy modifications of the tetrathiafulvalene (TTF) core is bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, Figure 1), in which two-dimensional conductivity was observed.[9] Moreover, organic superconductors are most commonly prepared from BEDT-TTF.

Dithiadiazafulvalenes (DTDAFs, Figure 1), which contain two nitrogen atoms in the tetraheterafulvalene core, are especially good electron donors ($E_{HOMO} = -3.916$ eV).[10] Despite this fact DTDAFs are among the less explored tetraheterafulvalenes due to their oxygen sensitivity,[11] which makes synthesis of many of them very challenging.

To the best of our knowledge, DTDAF with four sulfur or selenium atoms at the ends of the π-system, i.e. the diaza-BEDT-TTF analogue, has not been previously synthesized and its electric properties have not been explored.

In this paper we wish to report the first synthesis of bis(ethylenedithio)dithiadiazafulvalenes (BEDT-DTDAFs). The reaction of thiazolium salts with base is

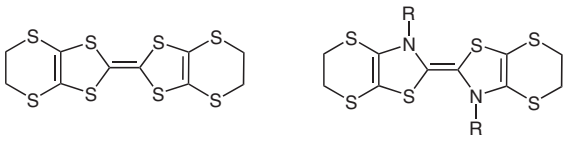
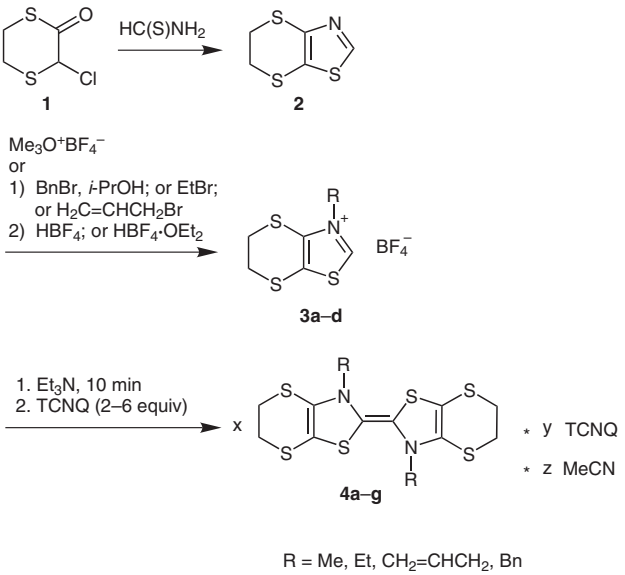


Figure 1



Scheme 1

one of the most commonly used methods for the preparation of dithiadiazafulvalenes,[8] hence the key intermediates for the preparation of BEDT-DTDAFs are the respective thiazolium salts **3a–d**.

We applied a modified Hantzsch synthesis to the preparation of 5,6-dihydro[1,4]dithiino[2,3-*d*]thiazole (**2**). 3-Chloro-1,4-dithian-2-one (**1**) was prepared according to a procedure described by Larsen and Lenoir.[12] Reaction of **1** with freshly prepared thioformamide affords **2** in moderate yields (Scheme 1). Of course, Hantzsch's synthesis has been applied to the preparation of thiazoles from α-halocarbonyl compounds and thioamides, and it is well known that reaction of α-halo esters with thioamides leads to thiazol-4(5*H*)-ones rather than to thiazoles.[13] Fortunately in our case the dehydration process was faster than 1,4-dithiane ring opening.

In the next step we alkylated **2** with alkyl bromides, followed by treatment with tetrafluoroboric acid, or trimethyloxonium tetrafluoroborate to give thiazolium tetrafluoroborate salts **3a–d**. The thiazolium salts could also be synthesized in one step by reaction of **1** with substituted thioformamides; we obtained thiazolium salts in this manner only in the case of 3-benzyl-5,6-dihydro[1,4]dithiino[2,3-*d*]thiazol-3-ium tetrafluoroborate (**3b**), but the yield did not exceed 12%. Phenylthioformamide in reaction with **1** did not give a thiazolium salt.

SYNTHESIS 2008, No. 5, pp 0696–0698
Advanced online publication: 08.02.2008
DOI: 10.1055/s-2008-1032167; Art ID: P12207SS

Table 1 BEDT-DTDAF·TCNQ Complexes **4a–g** Prepared

Compd	R	TCNQ (equiv)	Stoichiometry of complexes			Yield[a] (%)	Elemental analysis[a]	IR[b] ν_{CN} (cm^{-1})	Conductivity[c] ($mS \cdot cm^{-1}$)
			BEDT-DTDAF	TCNQ	MeCN				
4a	Me	2	3	8	1	37	$C_{134}H_{77}N_{39}S_{18}$	2194, 2160	3.23
4b	Me	4	3	16	1	64	$C_{230}H_{109}N_{71}S_{18}$	2176, 2153	3.54
4c	Et	2	3	10	2	29	$C_{166}H_{100}N_{48}S_{18}$	2194, 2165	8.06
4d	Et	4	3	16	0	48	$C_{234}H_{118}N_{70}S_{18}$	2200, 2153	7.23
4e	allyl	4	1	10	2	31	$C_{140}H_{64}N_{44}S_6$	2201, 2150	1.40
4f	Bn	2	3	16	2	29	$C_{268}H_{136}N_{72}S_{18}$	2196, 2154	2.56
4g	Bn	6	3	19	1	55	$C_{302}H_{145}N_{83}S_{18}$	2194, 2153	2.44

[a] All products had analysis C ±0.14, H ±0.40; N ±0.49; S ±0.22; except **4e**: C +0.66, H +1.07; N –1.14; S –1.14; **4f**: C –0.3, H +0.71; N –0.69; S –0.61.
[b] KBr.
[c] Conductivity for two-probe method, r.t., compaction.

The attempts to improve this reaction by facilitating the process with dehydrating agents, like thionyl chloride, 4-toluenesulfonic acid, or magnesium sulfate, according to a procedure similar to that of Salmond and Reid[14] failed.

Due to the sensitivity of dithiadiazafulvalenes to oxygen[11] all reactions of thiazolium tetrafluoroborate salts **3** with triethylamine were performed under argon in degassed solvents. We did not try to isolate the BEDT-DTDAFs as free compounds; tetracyanoquinodimethane (TCNQ) was immediately added to the mixture of the prepared BEDT-DTDAF in order to trap them as complexes **4a–g** (Table 1).

The position of ν_{CN} in the FTIR spectra of charge-transfer complexes of TCNQ can reflect the charge of TCNQ;[15] for the prepared complexes we usually observed two bands: a weak one in the region 2201–2189 and a strong one in the region 2165–2150, which would suggest the existence of TCNQ with a charge of up to 1.75, but such a charge value is obviously incorrect due to solid state environmental interaction that can considerably shift ν_{CN}.[16]

The electrochemical properties of BEDT-DTDAFs as well as superconductivity of the prepared complexes are currently being examined.

IR spectra were recorded from KBr pellets on a Bruker IFS66 infrared spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 500 MHz spectrometer using TMS as a reference. Elemental analyses were recorded on an Eager 200 instrument. Melting points are uncorrected. THF was distilled from potassium/benzophenone ketyl. CCl_4 and CH_2Cl_2 were dried with $CaCl_2$ and distilled. MeCN was dried with molecular sieves 4A, and four times frozen in a dry ice/acetone bath and degassed under vacuum (oil pump). All other commercially available reagents were used as received.

5,6-Dihydro[1,4]dithiino[2,3-*d*]thiazole (2)

NCS (8.01 g, 60 mmol) was added to a cooled soln of 1,4-dithian-2-one (5.36 g, 40 mmol)[12] in CCl_4 (150 mL) at 0 °C; the soln was stirred for 2 h. After filtration the solvent was removed at reduced pressure and the resulting oil was dissolved in anhyd THF (100 mL). The filtered soln was ice-cooled and a soln of $HC(S)NH_2$ in THF (200 mL) [freshly prepared from $HC(O)NH_2$ (9 g, 200 mmol) and P_2S_5 (8.88 g, 40 mmol)] was added dropwise; when the addition was complete (0.5 h) the mixture was stirred for 48 h. The solvent was removed under reduced pressure and the residue was made alkaline (to pH 10) with 2 M NaOH and extracted with EtOAc (5 × 50 mL). The combined organic phases were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was purified by chromatography (silica gel, CH_2Cl_2–hexane, 1:1); yield: 3.08 g (44%).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.56 (s, 1 H, CH), 3.41 (m, 2 H, CH_2), 3.27 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.05, 139.51, 117.24, 29.42, 28.80.

3-Methyl-5,6-dihydro[1,4]dithiino[2,3-*d*]thiazol-3-ium Tetrafluoroborate (3a)

To a soln of **2** (1.75 g, 10 mmol) in anhyd CH_2Cl_2 was added trimethyloxonium tetrafluoroborate (2.07 g, 14 mmol); the soln was stirred and heated to reflux for 24 h. The solvent was removed under reduced pressure and the residue was recrystallized twice (CH_2Cl_2–Et_2O); yield: 1.94 g (69%); mp 160–161 °C.

^1H NMR (500 MHz, acetone-d_6): δ = 10.09 (s, 1 H, CH), 4.23 (s, 3 H, NCH_3), 3.72 (m, 2 H, CH_2), 3.64 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, acetone-d_6): δ = 155.31, 135.60, 126.88, 40.27, 28.39, 28.11.

3-Benzyl-5,6-dihydro[1,4]dithiino[2,3-*d*]thiazol-3-ium Tetrafluoroborate (3b)

To a soln of **2** (2.62 g, 15 mmol) in *i*-PrOH (50 mL) was added every 48 h at total of BnBr (20.52 g, 120 mmol) in 5 portions. The soln was stirred and heated to reflux for 10 d. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 and washed with H_2O (5 × 30 mL). The aqueous layer was concentrated to 50 mL under reduced pressure and 50% HBF_4 (50 mL) was added. The precipitated crude salt **3b** was filtered and dried in vacuum; the product was recrystallized (CH_2Cl_2–Et_2O); yield: 3.20 g (60%); mp 137–139 °C.

^1H NMR (500 MHz, acetone-d_6): δ = 10.16 (s, 1 H, CH), 7.48 (m, 5 H, Ph), 5.82 (s, 2 H, NCH_2), 3.66 (m, 2 H, CH_2), 3.62 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, acetone-d_6): δ = 155.22, 135.33, 132.09, 129.72, 129.53, 129.09, 128.77, 57.23, 28.65, 28.49.

3-Allyl-5,6-dihydro[1,4]dithiino[2,3-*d*]thiazol-3-ium Tetrafluoroborate (3c)

Compound **2** (1.05 g, 6 mmol) was dissolved in allyl bromide (3 g, 24 mmol) and then sealed in a glass ampoule and heated to 62 °C for 48 h. The solvent was removed under reduced pressure and the residue was crystallized (MeOH–Et_2O). The crude thiazolium bromide (1.36 g, 4.6 mmol) was dissolved in CH_2Cl_2 and $HBF_4{\cdot}OEt_2$ (0.626 mL, 4.6 mmol) was added. Solvent was removed under reduced pressure and a new portion of CH_2Cl_2 was added and evaporation was repeated (5 ×). The crude product was recrystallized (acetone–Et_2O); yield: 1.36 g (75%); mp 78–80 °C.

^{1}H NMR (500 MHz, acetone-d_6): δ = 10.12 (s, 1 H, CH), 6.07–6.23 (m, *J* = 5.8, 10, 18 Hz, 1 H, CH_2=C*H*), 5.55 (dd, *J* = 10, 18, 2 H, C*H*$_2$=CH), 5.32 (d, *J* = 5.8 Hz, 2 H, NCH_2), 3.61–3.74 (m, 4 H, CH_2CH_2).

^{13}C NMR (125 MHz, acetone-d_6): δ = 154.98, 135.27, 129.45, 128.42, 122.81, 55.95, 28.83, 28.56.

3-Ethyl-5,6-dihydro[1,4]dithiino[2,3-*d*]thiazol-3-ium Tetrafluoroborate (3d)

Compound **2** (1.22 g, 7 mmol) was dissolved in EtBr (10.68 g, 98 mmol) and then sealed in a glass ampoule and heated to 62 °C for 21 d. The solvent was removed under reduced pressure and the residue was crystallized (MeOH–Et_2O). The crude thiazolium bromide (1.0 g, 3.52 mmol) was dissolved in CH_2Cl_2 and $HBF_4{\cdot}OEt_2$ (0.48 mL, 3.52 mmol) was added. Solvent was removed under reduced pressure and new portion of CH_2Cl_2 was added and evaporation was repeated (5 ×). The crude product was recrystallized (CH_2Cl_2–Et_2O); yield: 0.69 g (34%); mp 107–108 °C.

^{1}H NMR (500 MHz, acetone-d_6): δ = 10.11 (s, 1 H, CH), 4.62 (q, *J* = 7.3 Hz, 2 H, C*H*$_2$CH$_3$), 3.76 (m, 2 H, CH_2), 3.65 (m, 2 H, CH_2), 1.66 (t, *J* = 7.3 Hz, 3 H, CH_2C*H*$_3$).

^{13}C NMR (125 MHz, acetone-d_6): δ = 154.40, 134.66, 127.78, 49.80, 29.62, 29.46, 13.95.

Tetracyanoquinodimethane Charge Transfer Complexes of 3,3′-Dialkyl-5,5′,6,6′-tetrahydro-3*H*,3′*H*-[2,2′]bi[1,4]dithiino[2,3-*d*]thiazoles 4a–g; General Procedure

Compound **3** (0.5 mmol) was dissolved under argon in thoroughly degassed MeCN (10 mL). Et_3N (51 mg, 0.5 mmol) was added to a stirred soln, a deep red color appeared immediately. After 10 min a soln of TCNQ (102 mg, 0.5 mmol, or 204 mg, 1 mmol, or 306 mg, 1.5 mmol) in MeCN (20, 40, or 60 mL) was added. After 3 h the soln was concentrated to one fifth of its volume and refrigerated for 24 h. The precipitate was filtered, washed with MeCN (1 mL) and Et_2O (2 mL), and dried in a vacuum desiccator to yield **4a–g** (Table 1).

References

(1) Ferraris, J.; Cowan, D. O.; Walatka, V. Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.
(2) Geiser, U.; Schlueter, J. A. *Chem. Rev.* **2004**, *104*, 5203.
(3) Shibaeva, R. P.; Yagubskii, E. B. *Chem. Rev.* **2004**, *104*, 5347.
(4) Kobayashi, A.; Fujiwara, E.; Kobayashi, H. *Chem. Rev.* **2004**, *104*, 5243.
(5) Kobayashi, H.; Cui, H. *Chem. Rev.* **2004**, *104*, 5265.
(6) Kobayashi, A.; Tanaka, H.; Kobayashi, H. *J. Mater. Chem.* **2001**, *11*, 2078.
(7) Cowan, D. O.; McCullough, R.; Bailey, A.; Lerstrup, K.; Talham, D.; Herr, D.; Mays, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, 67; 277.
(8) Lorcy, D.; Bellec, N. *Chem. Rev.* **2004**, *104*, 5185.
(9) (a) Saito, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 354. (b) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, S.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneaul, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209. (c) Yamochi, H.; Komatsu, T.; Matsukawa, N.; Saito, G.; Mori, T.; Kusunoki, M.; Sakaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 11319. (d) Geiser, U.; Schlueter, J. A.; Wang, H. H.; Kini, A. M.; Williams, J. M.; Sche, P. P.; Zakowicz, H. I.; VanZile, M. L.; Dudek, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 9996.
(10) Eid, S.; Guerro, M.; Roisnel, T.; Lorcy, D. *Org. Lett.* **2006**, *8*, 2377.
(11) (a) Bssaibis, M.; Robert, A.; Lemagueres, P.; Ouahab, L.; Carliere, R.; Tallec, A. *J. Chem. Soc., Chem. Commun.* **1993**, 601. (b) Tonnos, G. V.; Baker, M. G.; Wang, P.; Lakshmikantham, M. V.; Cava, M. P.; Metzger, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 8528.
(12) Larsen, J.; Lenoir, C. h. *Synthesis* **1989**, 134.
(13) Metzger, J. V.; Katritzky, A. R. *Comprehensive Heterocyclic Chemistry*, Chap. 4.19, Part 4B, Vol. 6; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon: Oxford, **1983**, 235–333.
(14) Reid, D. H.; Salmond, W. G. *J. Chem. Soc. C* **1966**, 686.
(15) Chappel, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.
(16) Meneghetti, M.; Pecile, C. *J. Chem. Phys.* **1986**, *84*, 4149.