4a,6,7,8a-Tetrahydro-1,3-dithiolo[4′,5′:5,6]-1,4-dithiino-[2,3-*b*]-1,4-dithiine-2-thione as a precursor for synthesis of new organic π-donors

R. V. Pisarev, V. V. Kalashnikov, A. I. Kotov, and E. B. Yagubskii*

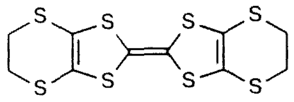
Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

[2+4]-Cycloaddition of 2,3-dihydro-1,4-dithiine and oligomeric 1,3-dithiol-2,4,5-trithione results in the formation of 4a,6,7,8a-tetrahydro-1,3-dithiolo[4′,5′:5,6]-[1,4]dithiino[2,3-*b*]-1,4-dithiine-2-thione, which is a precursor for synthesis of new organic π-donors.

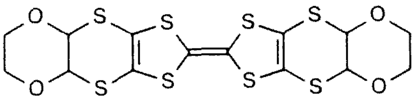
Key words: [2+4]-cycloaddition; 2,3-dihydro-1,4-dithiine; modification; bis(ethylenedithio)tetrathiafulvalene; π-donor.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) plays a special role among organic π-donor molecules. Radical-cation salts of ET form the widest class of organic molecular superconductors.[1,2] The number of superconducting salts of the ET family grows continuously, and their critical temperature of superconduction transition has reached 12.8 K.

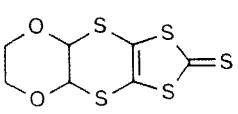
Chemical modification of the ET molecule is one of the main directions of the synthetic search for new organic superconductors. This trend is of great significance for establishment of correlations between the molecular structure of a donor and the electroconducting properties of radical-cation salts. One of the possibilities of this modification is the substitution of terminal ethylene fragments of the ET molecule for six-membered heterocycles.[3]



BEDT-TTF (ET)



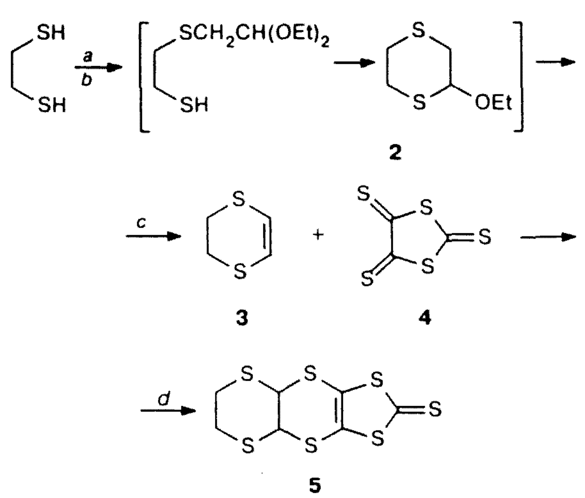
BDDT-TTF



1

We have previously synthesized cycloadduct **1**, which was used for synthesis of 4,5;4′,5′-bis(1,4-dioxane-2,3-diyldithio)tetrathiafulvalene (BDDT-TTF) by [2+4]-cycloaddition of 1,4-dioxene and oligomeric 1,3-dithiol-2,4,5-trithione $(C_3S_5)_x$.[3,4] In development of this direction of synthetic search for new π-donor derivatives of ET, we obtained precursor (**5**) of the sulfur analog of BDDT-TTF (Scheme 1).

Scheme 1



Reagents and conditions. *a.* NaOEt, EtOH, 25 °C. *b.* $BrCH_2CH(OEt)_2$, EtOH, 50 °C. *c.* TsOH, PhMe, Δ. *d.* $CHCl_3$, Δ.

2,3-Dihydro-1,4-dithiine (**3**), which was necessary for this purpose, was synthesized by the modified procedure[5] at two stages. We have established that compound **3** can be prepared without isolation of intermediate **2**. It is noteworthy that this method for the synthesis of compound **3** is substantially simpler and more conve-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 775—776, March, 1996.

1066-5285/96/4503-0735 $15.00

nient than usually used multi-stage schemes.[6] The diene component (**4**) was obtained by the procedure described previously.[7]

The structure of compound **5** was determined on the basis of the data of spectral and elemental analyses. The mass spectrum exhibits a peak with *m/z* 314 assigned to the molecular ion and an intense peak with *m/z* 118. The latter is assigned to the $C_4H_6S_2^+$ species and corresponds to retrodiene decomposition of the molecular ion observed for the oxygen analog of **1** as well.

The UV spectrum of compound **5** exhibits two absorption bands as in the case of cycloadduct **1**. However, the positions of the maxima in the spectrum of compound **5** are shifted to a longer-wave region compared to that of compound **1**.

The IR spectrum of compound **5** is close to that of the oxygen analog. In particular, this spectrum contains an intense band at 1055 cm^{-1}, which is likely related to the vibration of the C=S bond, and a band at 1489 cm^{-1} assigned to the vibration of the C=C bond. The position of maxima of the majority of the bands in the spectrum of compound **5** are shifted by 5 to 20 cm^{-1} compared to those of compound **1**.

Experimental

Mass spectra were obtained on a Finnigan MAT instrument (EA, 50 eV). UV spectra of solutions in $CHCl_3$ were recorded on a Specord M40 UV-VIS spectrophotometer, and IR spectra were recorded on a Specord-75 IR spectrophotometer in pellets with KBr. ^1H NMR spectra were recorded on a Bruker CXP-200 spectrometer.

2,3-Dihydro-1,4-dithiine (3). A solution of EtONa prepared from sodium metal (5.75 g, 0.25 mol) and anhydrous EtOH (130 mL) was added dropwise for 1 h to a solution of 1,2-ethanedithiol (23.55 g, 0.25 mol) in 65 mL of anhydrous EtOH. Bromoacetaldehyde diethyl acetal (49.3 mL, 0.25 mol) was added dropwise to the solution obtained upon stirring (Ar) for 40 min. The reaction mixture was heated to 45—50 °C with stirring (Ar) for 1.5 h and was then left to stand for ~12 h at 20 °C. A precipitate formed was filtered off and washed with diethyl ether. The filtrate and ether extracts were united, the solvent was distilled off, and the residue formed was distilled *in vacuo*, collecting a fraction over a wide b.p. range of 105—165 °C (2 Torr). The fraction obtained (10.8 g) was dissolved in 100 mL of anhydrous toluene, and *p*-toluenesulfonic acid monohydrate (0.95 g, 0.005 mol) was added. The mixture was refluxed using an efficient column to slowly distill off the ethanol formed. After cessation of ethanol formation, the mixture was cooled, neutralized with solid K_2CO_3, and distilled *in vacuo*. Compound **3** (5.22 g, 17.7 % calculated per initial 1,2-dithiol) was obtained as an almost colorless liquid with b.p. 75—77 °C (8 Torr), n_D^{25} 1.6292. ^1H NMR, δ: 3.20 (t, 4 H), 6.11 (d.d, 2 H). *Cf.* Ref. 5: b.p. 101 °C (29 Torr), n_D^{25} 1.6295. Found (%): C, 40.81; H, 5.18; S, 54.44. $C_4H_6S_2$. Calculated (%): C, 40.64; H, 5.12; S, 54.24.

4a,6,7,8a-Tetrahydro-1,3-dithiolo[4′,5′:5,6]-1,4-dithiino[2,3-*b*]-1,4-dithiine-2-thione (5). 2,3-Dihydro-1,4-dithiine **3** (0.95 g, 0.008 mol) was added to a suspension of compound **4** (2.08 g, 0.0106 mol) in 100 mL of $CHCl_3$. A reaction mixture was refluxed with stirring (Ar) for 10 h. A precipitate was filtered off and washed with hot $CHCl_3$. A filtrate was evaporated almost to dryness, ethanol was added, and a mixture was treated with active carbon. The precipitate formed was recrystallized from ethanol. Compound **5** (0.13 g, 5 %) was obtained as yellow microcrystals with m.p. 193—194 °C (from ethanol). IR (KBr), ν/cm^{-1}: 443 w, 468 s, 517 s, 557 w, 633 w, 676 m, 710 m, 760 s, 791 m, 810 m, 863 s, 880 w, 895 m, 925 m, 1000 m, 1018 sh, 1030 m, 1055 v.s, 1122 m, 1135 w, 1162 m, 1175 m, 1214 w, 1243 m, 1268 w, 1293 m, 1400 s, 1489 s. UV ($CHCl_3$), λ_{max}/nm: 280; 408. Mass spectrum, *m/z*: 314 [M^+], 118 [$C_4H_6S_2^+$], 76 [CS_2^+]. Found (%): C, 27.00; H, 1.94; S, 70.81. $C_7H_6S_7$. Calculated (%): C, 26.73; H, 1.92; S, 71.35. Molecular mass 314.54.

The authors are grateful to M. G. Kaplunov and G. A. Krasochka for help in spectral studies and for helpful discussion of the results obtained. The work was financially supported by the International Science Foundation (Grant RF 2300).

References

1. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, A. M. Kini, and M. H. Whangbo, *Organic superconductors*, Prentice Hall, Englewood Cliffs, NJ, 1992.
2. E. B. Yagubskii, *Mol. Cryst. Liq. Cryst.*, 1993, **230**, 139.
3. A. I. Kotov, C. Faulmann, P. Cassoux, and E. B. Yagubskii, *J. Org. Chem.*, 1994, **59**, 2626.
4. C. Faulmann, P. Cassoux, A. I. Kotov, and E. B. Yagubskii, *Acta Crystallogr.*, 1995, **C51**, 149.
5. W. E. Parham, J. Heberling, and H. Wynberg, *J. Am. Chem. Soc.*, 1955, **77**, 1169.
6. R. Kato, H. Kobayashi, and A. Kobayashi, *Synth. Met.*, 1991, **41—43**, 2093.
7. O. Ya. Neiland, Ya. Ya. Katsens, and Ya. N. Kreitsberga, *Zh. Org. Khim.*, 1989, **25**, 658 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].

Received November 25, 1995