Tetrahedron Letters, Vol. 33, No. 7, pp. 973-976, 1992
Printed in Great Britain

0040-4039/92 $3.00 + .00
Pergamon Press plc

# NEW LONG–CHAIN TETRATHIAFULVALENE DERIVATIVES WITH A DIACETYLENE GROUP

**V.Yu.Khodorkovsky [1], G.V.Tormos [1], O.Ya.Neilands [1]***
**N.V.Kolotilo [2] and A.Ya.Il'chenko [2]**

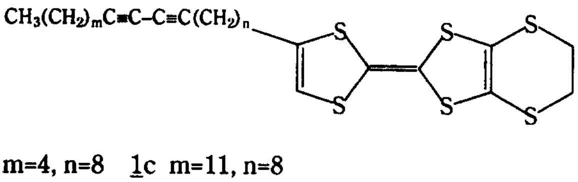
[1] Riga Technical University, 1 Kalku St., 226355 Riga, Latvia
[2] Institute of Organic Chemistry, 18 Murmansk St.,
255660 Kiev, Ukr. SSR

**Abstract:** The multi–stage synthesis of new long–chain tetrathiafulvalene derivatives containing a diacetylene group at different distances from tetrathiafulvalene moiety — 2–(tetracosa–9, 11–diynyle)–, 2–heptadeca–9, 11–diynyle)– and 2–(nonadeca–4,6–diynyle)– 6,7–tetrathiafulvalene is described.

Recent developments in the field of creating conducting Langmuir–Blodgett films based on surface–active charge–transfer complexes and ion–radical salts of organic electrondonors and acceptors have stimulated interest in the synthesis of long-chain substituted derivatives of tetrathiafulvalene (TTF)[1,2]. The complexes of e.g. heptadecyldimethyl TTF[3] and hexadecyl BEDT TTF[4] have proved[5] to give relatively stable conducting LB films.

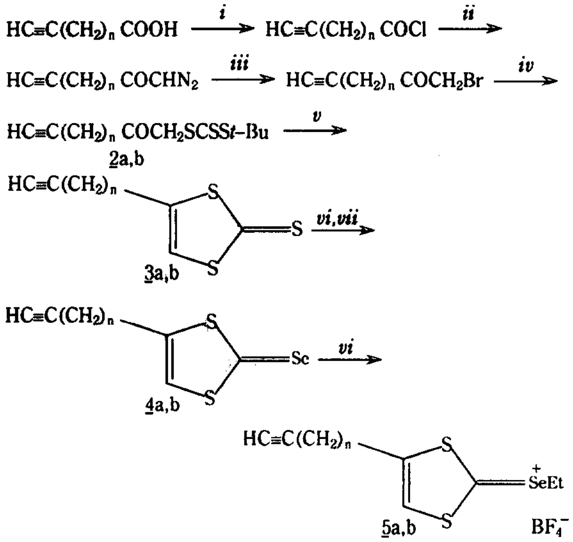
On the other hand, the diacetylenic compounds have attracted much attention due to their unique ability to form highly regular polymers upon irradiation which led us to the idea of combining the two types of compounds in the same molecule.

We now report the synthesis of new long-chain TTF derivatives 1 a,b,c containing the diacetylene group at different distances from the TTF moiety.



1a m=11, n=3  1b m=4, n=8  1c m=11, n=8

The multi-stage synthesis of the substances were carried out starting from hexynoic and undecynoic acids as shown in Scheme 1.



*i* $SOCl_2/CHCl_3$; *ii* $CH_2N_2$; *iii* HBr; *iv* Na SCSS*t*-Bu;

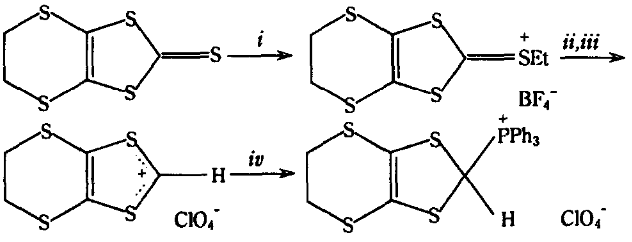
*v* $CF_3COOH/AcOH$; *vi* $BF_3 \cdot Et_2O/HC(OEt)_3$; *vii* $NaHSe/H_2O$

Scheme 1

The usual chloroanhydride — diazoketone — bromoketone sequence gave derivatives 2a,b (95–98% total yield). Reactions with sodium *t*-butyltrithiocarbonate and subsequent cyclization with trifluoroacetic acid and *p*-toluenesulfonic acid as a catalyst[6] gave poor yields (8–10%) of the desired 1,3-dithiole-2-thione derivatives 3a,b, the formation of a great amount of red-brown tar was observed. In the absence of p-toluenesulfonic acid, however, the cyclization appeared to proceed more smoothly in both cases and thiones 3a,b were obtained in 60–70% yield as yellow solids and converted[7] to the corresponding orange 1,3-dithiole-2-selenones 4a,b (72–86% yield). 2-Ethylseleno-1,3-dithiolium tetrafluoroborates 5a,b were obtained by alkylation of 4a,b and were used without further purification.

4,5-Ethylenedithio-1,3-dithiole-2-triphenylphosphonium perchlorate 6 was obtained from 4,5-ethylenedithio-1,3-dithiole-2-thione as shown in Scheme 2 (total yield 72%)[8].

A similar method was used by other group for the synthesis of the corresponding tetrafluoroborate[9].



6

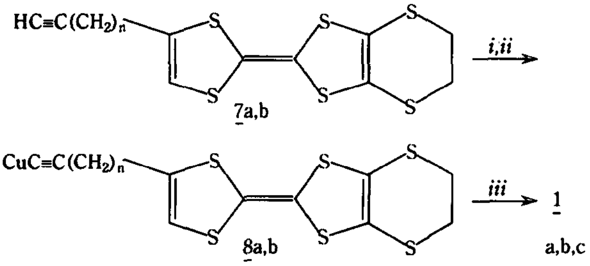
*i* $BF_3 \cdot Et_2O/CH(OEt)_3$; *ii* $NaBH_4/CH_3CN$;
*iii* $HClO_4/Ac_2O$; *iv* $PPh_3/CH_3CN/EtOH$

Scheme 2

Compounds 5a,b and 6 were coupled by the general method, suggested by us for the preparation of unsymmetrical TTFs. The unsymmetrical products 7a,b were obtained in 72–77% yields as orange leaflets. Recently we reported a synthesis and crystal structure of 2,3-vinylenedithio-6,7-ethylenedithio TTF as another example of using this method[8]. Experimental details for the series of unsymmetrical TTFs will be published separately.

All our attempts to obtain the diacetylene derivatives from 7a,b by Cadiot-Chodkiewicz reaction have been unsuccessful. The cuprous salts 8a,b were however obtained as yellow solids in good yields by subsequent treatment of 7a,b with butyllithium and cuprous chloride in THF as outlined in Scheme 3.

Reactions of 8a,b with corresponding bromoalkynes in pyridine gave the desired TTF derivatives 1a,b,c as orange solids[10] soluble in non-polar solvents, sparingly soluble in acetonitrile.



*i* BuLi/THF; *ii* CuCl; *iii* $CH_3(CH_2)_mC{\equiv}CBr/Py$

Scheme 3

Cyclic voltammograms in DMF showed two reversible oxidation peaks (0.48 and 0.68 V, vs.Ag/AgCl). The ability of 1a,b,c to form stable films is now under study.

**Acknowledgements:** The authors are grateful to A.Edzina for oxidation potentials measurements and to A.Jansone for help with the preparation of the manuscript.

## References and notes.

1. J.Richard, M.Vandevyver, A.Barraud, R.Lapouyade, P.Delhaes, J.F.Jacquinot, M.Roulliay, J.C.S.Chem.Comm. 754 (1988).

2. A.S.Dhindsa, J.P.Badya, M.R.Bryce, M.C.Petty, A.J.Moore, Yu.M.Lvov, J.C.S. Chem. Comm. 970 (1990).

3. Ya.Kreicberga, D.Bite, V.Kampar, R.Kampare, O.Neilands, J.Org.Chem. (USSR), 17,10055 (1981).

4. V.Khodorkovsky, G.Pukitis, A.Puplovsky, O.Neilands, Chem.Heterocycl.Comp. (USSR), 131 (1990).

5. T.Berzina, P.Sotnikov, V.Troitsky, O.Neilands, G.Pukitis, V.Khodorkovsky, 2 Int.Conf.Molec.Electronics and Biocomput., Abstract, Moscow, 1989, p.12.

6. N.F.Haley, M.W.Fichtner, J.Org.Chem., 45, 175 (1980).

7. V.Khodorkovsky, Ya.Kreicberga, K.Balodis, O.Neilands, Izv.AN Latv.SSR, Ser.Khim., 120 (1988).

8. V.Korotkov, R.Shibaeva, K.Balodis, V.Khodorkovsky, O.Neilands, Crystallography (USSR), 36, 113 (1991).

9. A.J.Moore, M.R.Bryce, Synthesis, 26 (1991).

10. 1a - m.p.43–45°, nmr($CDCl_3$): 0.83(t,$CH_3$), 1.2–1.7(m,11$CH_2$), 2.15–2.48(m,3$CH_2$), 3.23(s,2$CH_2$), 5.92(s,CH). 1b - m.p.72–74°, nmr($CDCl_3$): 0.83(t,$CH_3$), 1.23 - 1.69(m,9$CH_2$), 2.16 - 2.32 (m,3$CH_2$), 3.22(s,2$CH_2$), 5.83(s,CH). 1c - m.p. 52–54°, nmr($CH_2Cl_2$) 0.81(t,$CH_3$), 1.18 - 1.55 (m,16$CH_2$), 2.14–2.30(m,3$CH_2$), 3.23 (s,2$CH_2$), 5.81(s,CH).

(Received in UK 9 December 1991)