Some novel substituted tetrathiafulvalenes: alkylation of sodium salts of 4-sulfanyl-5-alkylcarboxymethylthio-1,3-dithiole-2-thione

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A number of new substituted tetrathiafulvalenes that can be useful in constructing molecular films by Langmuir–Blodgett technology have been synthesised by successive chemical transformations of 3-oxo-2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-ene-8-thione.

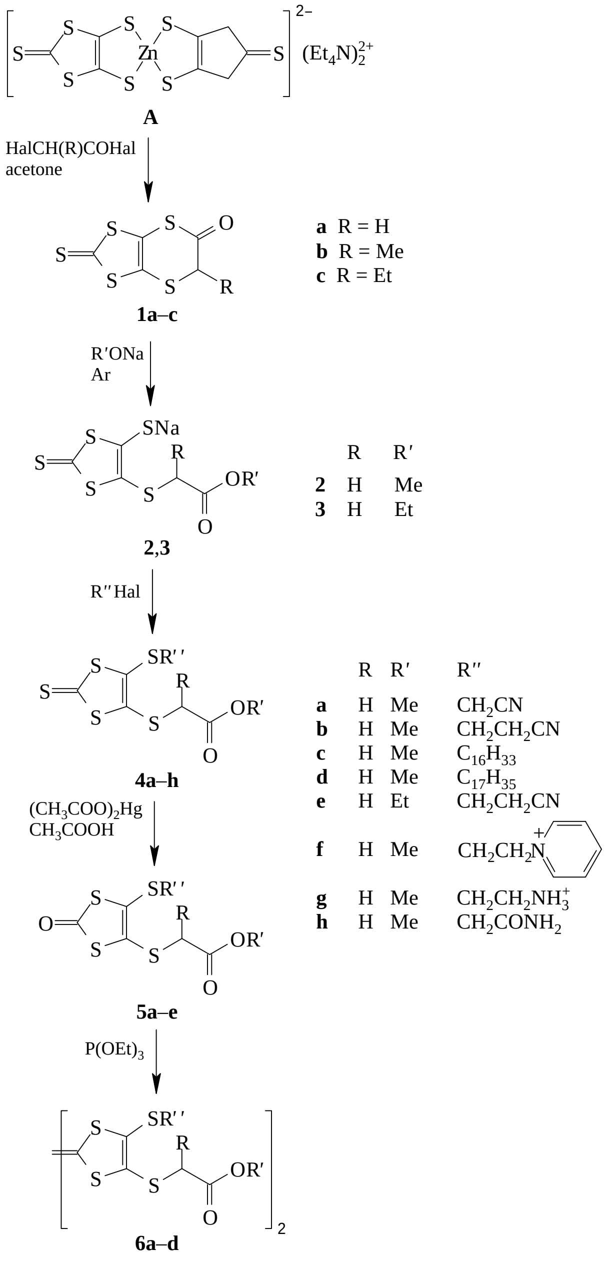
Studies dealing with the synthesis and properties of various 1,3-dithiole-2-thiones are being constantly carried out, because there is ongoing interest in obtaining new radical-cation salts and charge-transfer complexes of the tetrathiafulvalene series, which are well known as low-dimensional organic semiconductors, metals and superconductors.[1] The design and synthesis of various substituted π-donors are among the central problems in this field of organic chemistry. It seems of considerable interest to find routes for the synthesis of various tetrathiafulvalene derivatives incorporating functional groups such as carboxyl, carbonyl, hydroxy, amino, alkoxycarbonyl, *etc.* or to collect all of these groups in the same molecule. All these functional groups influence to a certain extent the inter- and intra-stack interactions (for example, the formation of hydrogen bonds, changes in the van der Waals interactions, *etc.*) during the formation of radical-ion salts. This makes it possible to prepare conducting materials possessing new properties. In addition, the introduction of substituents of this type opens the way for the synthesis of compounds suitable for preparing Langmuir–Blodgett films; films based on tetrathiafulvalene derivatives exhibit the highest electrical conductivities among various films created on the water

Table 1 Compounds **4a**–**e**, **5a**–**e** and **6a**–**d**. Molecular formulae, yields, elemental analyses, melting points and IR and NMR spectral data.

Compound Formula	Yield (%)	Mp/°C	% S		IR ν/cm^{-1}	NMR δ ($CDCl_3$)
			Found	Calc.		
4a $C_8H_7NO_2S_5$	93.8	68–70	51.79	51.68	1058 (C=S), 2249 (CN), 1739 (COO–)	CD_3CN: 3.66 (s, 3H, OCH_3), 4.06 (s, 2H, SCH_2C), 4.20 (s, 2H, SCH_2CN)
4b $C_9H_9NO_2S_5$	60.7	69–73	49.33	49.46	1062 (C=S), 2245 (CN), 1735 (COO–)	3.71 (s, 3H, CH_3), 3.58 (s, 2H, SCH_2CO), 2.14 (t, 2H, CH_2), 3.04 (t, 2H, CH_2)
4c $C_{22}H_{38}O_2S_5$	68.5	35–37	32.15	32.42	1056 (C=S), 2249 (CN), 1739 (COO–)	0.87 (t, 3H, CH_3), 1.2 [s, 28H, $(CH_2)_{14}$], 2.1 (t, 2H, SCH_2), 3.52 (s, 2H, SCH_2CO), 3.71 (s, 3H, CH_3)
4d $C_{23}H_{40}O_2S_5$	65	59–60	31.50	31.43	1056 (C=S), 1726 (COO–)	CD_3CN: 0.81 (t, 3H, CH_3), 1.2 [s, 30H, $(CH_2)_{15}$], 3.12 (t, 2H, SCH_2), 3.57 (s, 2H, SCH_2CO), 3.71 (s, 3H, CH_3)
4e $C_{10}H_{11}NO_2S_5$	72	67–70	47.41	47.50	1050–1058 (C=S), 2248 (CN), 1726 (COO–)	1.24 (t, 3H, CH_3), 2.73 (t, 2H, CH_2), 2.96 (t, 2H, CH_2), 3.58 (s, 2H, SCH_2CO), 4.17 (q, 2H, CH_2)
4f $C_{13}H_{15}NIO_2S_5$	61	105–106	31.65	31.78	1062 (C=S), 1730 (C=O)	3.58 (s, 2H, CH_2), 3,67 (t, 2H,CH_2), 3.73 (s, 3H,CH_3), 4.80 (t, 2H, CH_2), 7.81 (m, Ar)
4g $C_8H_{13}INO_2S_5$	62	153–157	36.20	36.23	1070 (C=S), 1735 (C=O)	2.79 (t, 2H, CH_2), 3.59 (s, 2H,CH_2), 3.70 (s, 3H, CH_3), 4.75 (t, 2H, CH_2)
4h $C_8H_{11}NO_3S_5$	64	114–116	48.51	48.65	1060 (C=S)	CD_3CN: 3.73 (s, 3H, OCH_3), 3.69 (s, 2H, SCH_2C), 3.76 (s, 2H, SCH_2CO), 5.3 (s, 2H, NH_2)
5a $C_8H_7NO_3S_4$	53	oil	43.49	43.62	1731 (COO–), 1667 (C=O), 2248 (CN)	CD_3CN: 3.65 (s, 3H, OCH_3), 4.01 (s, 2H, SCH_2C), 4.23 (s, 2H, SCH_2CN)
5b $C_9H_9NO_3S_4$	58	45–48	41.53	41.64	1731 (COO–), 1667 (C=O), 2248 (CN)	2.49 (t, 2H, CH_2), 3.06 (t, 2H, CH_2), 3.57 (s, 2H, SCH_2CO), 3.71 (s, 3H, CH_3)
5c $C_{22}H_{38}O_3S_4$	75	33–35	27.24	27.36	1738 (COO–), 1665 (C=O), 2248 (CN)	0.82 (t, 3H, CH_3), 1.19 [s, 28H, $(CH_2)_{14}$], 2.89 (q, 2H, CH_3), 3.50 (s, 2H, SCH_2CO), 3.70 (s, 3H, CH_3)
5d $C_{23}H_{40}O_3S_4$	72	36–38	25.93	26.02	1738 (COO–), 1667 (C=O)	CD_3CN: 0.80 (t, 3H, CH_3), 1.15 [s, 28H, $(CH_2)_{14}$], 3.12 (q, 2H, CH_3), 3.52 (s, 2H, SCH_2CO), 3.68 (s, 3H, CH_3)
5e $C_{10}H_{11}NO_3S_4$	67	81–84	39.80	39.90	1731 (COO–), 1669 (C=O), 2246 (CN)	1.25 (t, 3H, CH_3), 2.78 (t, 2H, CH_2), 2.96 (t, 2H, CH_2), 3.58 (s, 2H, SCH_2CO), 4.15 (q, 2H, CH_2)
6a $C_{16}H_{14}N_2O_4S_8$	35.6	153–156	46.06	46.23	1725 (COO–), 2248 (CN)	3.54 (s, 4H, $2CH_2$), 3.58 (s, 4H, $2CH_2$) 3.72 (s, 4H, $2CH_2$)
6b $C_{18}H_{18}N_2O_4S_8$	38	156–158	43.92	44.01	1723 (COO–), 2248 (CN)	2.12 (t, 4H, $2CH_2$), 3.01 (t, 4H, $2CH_2$), 3.55 (s, 4H, $2SCH_2CO$), 3.72 (s, 6H, $2CH_3$)
6c $C_{44}H_{72}N_2O_4S_8$	31	35–37	26.93	27.01	1734 (COO–)	0.87 (t, 6H, $2CH_3$), 1.2 [s, 56 H, $2(CH_2)_{14}$], 2.1 (t, 4H, $2SCH_2$), 3.52 (s, 4H, SCH_2CO), 3.75 (s, 6H, CH_3)
6d $C_{46}H_{76}N_2O_4S_8$	65	34–36	26.11	26.24	1741 (COO–)	0.85 (t, 6H, CH_3), 1.22 [s, 60H, $2(CH_2)_{15}$], 2.1 (t, 4H, $2SCH_2$), 3.52 (s, 4H, $2SCH_2CO$), 3.75 (s, 6H, $2CH_3$)

surface.[1–3] Thus, these organic compounds act as building blocks in constructing TTF and the problem of their synthesis is very urgent.

3-Oxo-2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)ene-8-thione **1a** and its alkyl derivatives **1b**,**c** proved to be very convenient initial compounds in the synthesis of tetrathiafulvalenes containing functional groups and long-chain alkyl substituents. This is due to the following factors: (1) they can be readily prepared in large quantities from zinc complex **A** and the corresponding halo-derivatives;[4] (2) alkaline cleavage of these compounds readily occurs under ambient conditions to give intermediate salts (for example, **2**,**3**); the high reactivity of these compounds enables introduction of diverse substituents in their molecules.[5] These sodium salts, which are used subsequently as alcoholic solutions, were obtained by addition of 1,3-dithiole-2-thiones **1a**,**b** to alcoholic solutions of the corresponding sodium alkoxides at 20 °C under argon followed by addition of the corresponding halo-derivative. Most of these reactions require keeping the mixture for 5–10 min at 40 °C after the addition of all the reactants. The products were obtained in good yields (60–80%). Some of the newly obtained thiones **4a**–**e** were readily converted into the corresponding oxygen derivatives **5a**–**e** by oxidation with mercuric acetate in acetic acid or in its mixture with chloroform. A specific feature of the structures of the compounds obtained is that they are asymmetrical, *i.e.* their molecules contain two substituents with different chemical natures in the 4- and 5-positions. Thus, they permit preparation of tetrathiafulvalenes that cannot be obtained by any other method known at present. Heating of 1,3-dithiol-2-ones **5a**–**d** in triethyl phosphite for 15 min at 120 °C in an argon flow gave new tetrathiafulvalenes **6a**–**d** in high yields as orange crystals (thin needles).[†]



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[†] *General experimental details.* IR spectra were recorded on a Perkin-Elmer 1725X Fourier-Transform IR spectrometer (for KBr pellets); NMR spectra were measured on a Bruker WP-80-SY instrument using HMDS (hexamethyldisiloxane) as the internal standard. The zinc complex **A** was synthesised by a known procedure.[6]

4a. 1,3-Dithiole-2-thione **1a** (2.4 g, 0.01 mol) was added in portions in a flow of dry argon to a solution of sodium methoxide (obtained from 0.23 g, 0.01 mol of Na) in anhydrous methanol (40 ml). To the resulting solution of salt **2**, a small excess of choloroacetonitrile (0.8 g, 0.01 mol) was added dropwise, and the reaction mixture was heated under reflux for 5 min. The product precipitated after cooling was filtered off and recrystallised from methanol.

The compounds **4b**–**h** were prepared in a similar way.

5a. A mixture of **4a** (3.09 g, 0.01 mol) and mercuric acetate (3.23 g, 0.0102 mol) in 50–60 ml of acetic acid was heated under reflux until a black precipitate of HgS was formed completely. The precipitate was separated from the hot reaction mixture by filtration. Cold water was slowly added dropwise to the cooled solution of **5a**; the precipitate thus formed was collected and dried to give the product in a fairly pure state.

Compounds **5b**–**e** were synthesised in a similar way.

6a. Suspension of **5a** (1 g, 0.0034 M) in triethyl phosphite was heated for 10 min in a flow of dry argon. The solution gradually turned orange and upon cooling, crystals of **6a** precipitated. To ensure complete precipitation, methanol was added to the solution. The tetrathiafulvalene thus obtained was purified by recrystallisation from acetonitrile.

The same procedure was used to prepare the tetrathiafulvalenes **6b**–**d**.