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ORGANIC ELECTRONIC CONDUCTORS AND PRECURSORS - X.
SYNTHESIS OF 1,3-TETRATHIAFULVALENES BASED ON 1,3,5,7-TETRATHIA-s-INDACENE-2,6-DIONES

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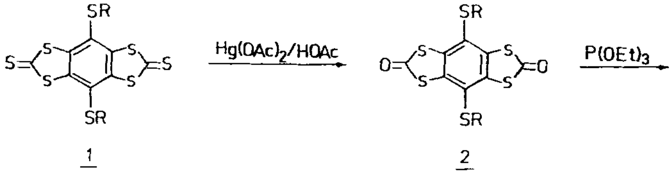
Abstract Desulfurization of 4,8-bis(alkylthio)-1,3,5,7-tetrathia-s-indacene-2,6-dithiones 1 leads to the corresponding diones 2 which are coupled to tetrathiafulvalenes (TTF) 3. Base induced opening of the dithiolone rings of 3 followed by alkylation gives the novel per(alkylthio)dibenzo-TTF 4.

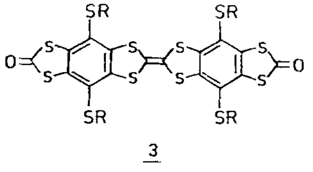
Aiming at increasing the intermolecular interaction between the tetrathiafulvalene (TTF) molecules in TTF charge-transfer complexes we were concerned with per(alkylthio) substituted dibenzo-TTF. Therefore we have synthesized the alkythio substituted 1,3,5,7-tetrathia-s-indacene-2,6-diones 2 as corresponding precursors.

The 4,8-bis(alkylthio)-1,3,5,7-tetrathia-s-indacene-2,6-dithiones [1] (1) were converted into the diones 2 in the usual way by desulfurization in glacial acetic acid using mercury(II) acetate. The diones 2 can be coupled to the tetrathiafulvalenes 3 in good yields.



1

2

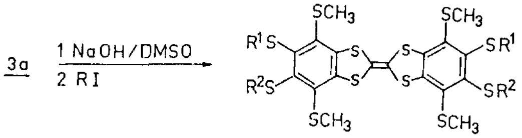


3

	R
a	CH_3
b	n-C_5H_{11}

The TTF 3a was obtained from the slight soluble dione 2a when boiling triethyl phosphite was used, the formation of the TTF 3b proceeds in refluxing acetonitrile in presence of triethyl phosphite.

From the TTF 3a new benzo-anellated tetrathiafulvalenes 4 were prepared. Base induced opening of the 1,3-dithiolone rings with sodium hydroxide in dimethylsulfoxide followed by alkylation leads to the per(alkylthio)dibenzo-1,3-tetrathiafulvalenes 4.



4

4	R^1	R^2
a	CH_3	CH_3
b	$-CH_2-$	

The compounds 3 and 4 obtained are sparingly soluble in conventional organic solvents. By electrochemical oxidation of the better soluble TTF 3b and 4a two half-wave potentials were determined (Table 1). The values are in accordance with the acceptor substitution of the dibenzo-TTF by an anellated dithiolone ring and substituted dibenzo-TTF, respectively (see ref.[2-5]). The first half-wave value corresponds to the formation of a cation radical, at higher potential further oxidation takes place to produce the dication.

Table 1 Cyclic Voltammetry of 3b and 4a

Compd.	$E_1^{ox}[V]$	$E_2^{ox}[V]$	Conditions
3b	0.90	1.20	SCE, 0.01 M TBAP, 1,2-dichloroethane
4a	0.74	1.09	SCE, 0.1 M TBAP, 1,2-dichloroethane

The chemical oxidizability of the TTF depends on the type of substitution. TTF 4a is oxidized by iodine, bromine or antimony pentachloride whereas the acceptor substituted dibenzo-TTF 3b is only oxidized by bromine or antimony pentachloride.

The spectroscopic data of the cation radical salts and the dication salts as well are assembled in Table 2.

Table 2 Spectroscopic data of the oxidation products of 3b and 4a

Compd.	λ_{max} [nm]			Solvent
	I_2	Br_2	$SbCl_5$	
$\underline{3b}^{+\cdot}$	-	760	770	$CHCl_3$
$\underline{3b}^{++}$	-	-	669	$CHCl_3$
$\underline{4a}^{+\cdot}$	825	829	830	$CH_2Cl\text{-}CH_2Cl$

Experimental·

Melting points were determined on a Boetius apparatus and are corrected. NMR spectra were recorded on a Bruker HX-90R. Mass spectral data were obtained on a VG ZAB-HSQ and Varian CH6. A Carl-Zeiss-Jena Specord M80 and M40 was used to record the IR and UV-VIS spectra, respectively.

4,8-Bis(methylthio)-1,3,5,7-tetrathia-s-indacene-2,6-dione (2a)

18 mmol (6.9 g) 1a and 72 mmol (22.9 g) mercury(II) acetate were stirred under reflux for 8 h in a mixture of 500 mL glacial acetic acid and 100 mL 1,2-dichloroethane. The hot mixture was filtered. After cooling, the precipitated colourless needles were isolated and recrystallized from 1,2-dichlorobenzene to give 4.5 g of the dione 2a in 71% yield. - m.p.· 299-302°C, MS· $M^+=350$, IR(KBr) [cm^{-1}] :ν_{CO} 1630(s), 1690(m). - UV ($CHCl_3$)λ_{max} [nm](logε)· 252(4.50), 268sh(4.2), 300sh(3.6), 334(3.69), 345(3.80). Anal. Calcd. for $C_{10}H_6O_2S_6$ (350.51): C, 34.26, H, 1.73, S, 54.88. Found C, 34.45, H, 1.85, S, 54.79 %.

4,8-Bis(pentylthio)-1,3,5,7-tetrathia-s-indacene-2,6-dione (2b)

2b was prepared as described above in glacial acetic acid (reaction time 3 h). Yield 6.3 g (76%), colourless needles, m.p. 143-144°C, MS $M^+=462$, ^{13}C-NMR (90 MHz) ($CDCl_3$) δ [ppm] 22.2, 27.3, 33.7, 38.7, 123.6, 139.2, 186.2. - IR(KBr) [cm^{-1}] ·ν_{CO} 1650(s), 1715(m). - UV ($CHCl_3$)λ_{max} [nm](logε)· 253(4.53), 268sh(4.3), 300sh(3.6), 334(3.67), 345(3.80). Anal. Calcd. for $C_{18}H_{22}O_2S_6$ (462.72) C, 46.72, H, 4.79, S, 41.57. Found· C, 47.00, H, 4.59, S, 41.70 %.

6,6'-Dioxo-4,4',8,8' -tetrakis(methylthio)- $\Delta^{2,2'}$-bi-1,3,5,7-tetrathia-s-indacene (3a)

0.34 mmol (0.12 g) 2a were stirred under reflux in 10 mL triethyl phosphite for 30 min. The yellow precipitate was filtered off, washed with methanol, ether and dried. - Yield 0.11 g (96%), m.p. >360°C, MS· $M^+=668$, IR(KBr) [cm^{-1}] ν_{CO} 1652(s), 1690(m). - UV-VIS ($CHCl_3$)λ_{max} [nm]· 263, 303, 413. Anal. Calcd. for

$C_{20}H_{12}O_2S_{12}$ (669.02) C, 35.90; H, 1.81, S, 57.51. Found: C, 35.77, H, 2.01; S, 57.45 %.

6,6'-Dioxo-4,4',8,8' -tetrakis(pentylthio)- $\Delta^{2,2'}$-bi-1,3,5,7-tetrathia-s-indacene (3b)

0.86 mmol (0.4 g) 2b were dissolved in 40 mL boiling acetonitrile and triethyl phosphite (0.75 mL) was added. After refluxing the mixture for 15 h, the precipitate was filtered off, washed with acetonitrile and ether. - Yield: 0.33 g (86%); yellow orange needles, m.p.: 343-345°C, IR(KBr) $[cm^{-1}]$: ν_{co} 1655(s), 1695(m). - UV-VIS ($CHCl_3$) λ_{max} [nm](logε): 264(4.75), 303(4.60), 413(4.10). Anal. Calcd. for $C_{36}H_{44}O_2S_{12}$ (893.43): C, 48.39, H, 4.96; S, 43.06. Found: C, 48.05, H, 4.78, S, 42.76 %.

Per(methylthio)dibenzotetrathiafulvalene (4a)

0.45 mmol (0.3 g) TTF 3a were dissolved in a hot suspension of 10 mmol (0.4 g) sodium hydroxide in 15 mL DMSO, after cooling down to room temperature 12 mmol (0.75 mL) methyl iodide was added and the precipitate was filtered off, washed with water, methanol and ether. - Yield: 0.27 g (90%); yellow orange crystals, m.p.: 302-304°C, MS M^+=672, ^1H-NMR ($CDCl_3$) δ [ppm]: 2.45 s, 2.47 s. - UV-VIS ($CHCl_3$) λ_{max} [nm](logε): 409(4.02). Anal. Calcd. for $C_{22}H_{24}S_{12}$ (673.13): C, 39.25, H, 3.59, S, 57.16. Found: C, 39.01, H, 3.52, S, 57.41 %.

4,4'8,8' -Tetrakis(methylthio)- $\Delta^{2,2'}$-bi-1,3,5,7-tetrathia-s-indacene (4b)

Using the same procedure as described for TTF 4a, 4b was obtained with 7.5 mmol (0.6 mL) methylene iodide as alkylation reagent. - Yield: 0.21 g (73%), yellow orange crystals, m.p.:>360°C, MS: M^+=640, UV-VIS ($CHCl_3$) λ_{max} [nm]: 416. Anal. Calcd. for $C_{20}H_{16}S_{12}$ (641.05): C, 37.47, H, 2.52, S, 60.01. Found: C, 37.59, H, 2.54, S, 59.64 %.

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