Synthesis of a New Polyfluorinated Vinylogue of Tetrathiafulvalene through 1,3-Dipolar Cycloaddition of Ethyl β-Bromoperfluorodithiocrotonate with Dimethyl Acetylenedicarboxylate

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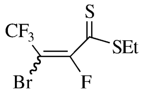
Abstract: The ethyl ester of β-bromoperfluorodithiocrotonic acid reacts with dimethyl acetylenedicarboxylate to give 1,4-difluoro-2,3-bis(trifluoromethyl)-but-2-ene-1,4-diylidene-2,2′-bis(4′,5′-dicarbomethoxy-1′,3′-dithiole) (**4**), a new type of vinylogue of tetrathiafulvalene. The thermal transformations of this compound lead, depending on the temperature, to the formation of the cyclization products: 11,14-difluoro-2,3,8,9-tetra(carbomethoxy)-12,13-bis(trifluoromethyl)-1,4,7,10-tetrathiadispiro[4.0.4.4]tetradeca-2,8,11,13-tetraene (**8**) or 5,8-difluoro-6,7-bis(trifluoromethyl)-2,3-bis(carboxymethyl)-1,4-benzodithiine (**11**).

Keywords: alkynes · cycloaddition · dithiocrotonic acid · sulfur heterocycles · tetrathiafulvalene

Introduction

Within the framework of a programme devoted to the chemistry of perfluoroketene dithioacetals, we have recently reported on the synthesis and some aspects of the reactivity of a new type of unsaturated dithiocarboxylic acid derivative: ethyl β-bromoperfluorodithiocrotonate (**1**).[1] In contrast to non-fluorinated dithiocrotonates, which are unstable and exhibit both heterodiene and C=C dienophilic characters,[2] compound **1** proved to be stable and exhibited selective C=S dienophilic behaviour. The ability of dithioesters to act as 1,3-dipoles in [3+2]-cycloaddition reactions with dimethyl acetylenedicarboxylate (DMAD) is well documented.[3] In the fluorinated series, we have recently reported such a cycloaddition from a 1,2-dithiole-3-thione, which led to an original 4,5-dicarbomethoxy-1,3-dithiole derivative.[4] These observations, associated with the great interest of dithiole derivatives, prompted us to study the reactivity of our crotonic compound **1**, in spite of its apparent electron-deficient character, with DMAD. This research led to unexpected results: the formation of a new polyfluorinated vinylogue of tetrathiafulvalene (TTF), itself being an intermediate towards new thiaheterocyles. This paper is a full account of these unprecedented reactions and products.



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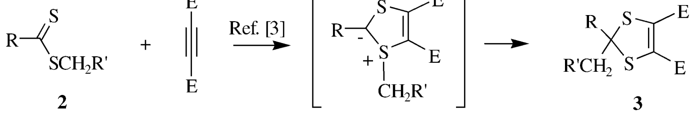
Results and Discussion

The reaction of non-fluorinated allyl or benzyl dithiocarboxylates **2** with DMAD has been reported to give dithioacetals **3**, as a result of a dipolar cycloaddition leading to intermediate ylides that rearrange to the final compounds **3** (Scheme 1).[3]



R' = Ph, CHCH$_2$, E = CO$_2$Me

Scheme 1.

The electrofugal character of the S-alkyl group plays an important role in this pathway. Owing to the unsaturated and perhalogenated structure of **1**, and to the poor electrofugal

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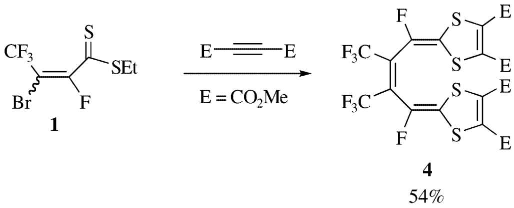
DOI: 10.1002/chem.200304839

property of the ethyl group, we were very interested in investigating its behaviour.

Compound **1** reacted easily and cleanly with DMAD at room temperature, to give violet crystals which exhibited poorly informative spectra. Crystallisation (AcOEt/petroleum ether) allowed the isolation of 54 % of a pure compound. X-ray diffraction analysis disclosed that a dipolar cycloaddition had indeed occurred, but leads to the quite unexpected structure **4**, which includes two dithiocrotonic–DMAD adduct units (Scheme 2).



Scheme 2.

Compound **4** is an unprecedented vinylogous derivative of TTF. TTF and its derivatives represent an important group of compounds that are able to generate conducting or superconducting materials.[5] One of the modern trends in the chemistry of TTF derivatives is the spatial extension of TTF donors, in particular by separating the 1,3-dithio-2-ylidene fragments by conjugated blocks such as mono- or polyolefinic, acetylenic, aromatic or heteroaromatic π-systems.[6] The insertion of the unsaturated spacer between the two dithiole units was generally performed by using Wittig or Wittig–Horner reactions, or by reductive or desulfurazing couplings of aldehydes or thioaldehydes. Most of the vinylogous derivatives of TTF synthesised so far contain either an unsubstituted spacer or one substituted by alkyl or aryl groups. Except for one compound bearing two trifluoromethyl groups on a monoolefinic spacer,[7] other examples of fluorine-containing TTF are fluorinated on the dithiole moiety.[8] Compound **4** has an interesting structure that exhibits both the π-donor character of the vinylic fluorine atoms and the withdrawing character of the trifluoromethyl groups, and will deserve further physicochemical investigation.

The structure of the compound **4** in the solid state, as determined by single-crystal X-ray diffraction, is described in Figure 1 and Table 1. CF$_3$ substituents have a *cis* orientation relative to the central C5=C5′ double bond. The =C–C=C–C= bond system is noticeably nonplanar (the torsion angles C1-C4-C5-C5′ and C4-C5-C5′-C4′ being 15.4 and 45.8°, whereas the S1-C1-C4-C5 torsion angle is only 3.0°). The heterocycle S1-S2-C1-C2-C3 is planar within 0.01 Å, and the C7-O1-O2 and C9-O3-O4 groups are twisted out of this plane by 58.6 and 24.4°. The dithiole cycles in **4** are noticeably non-coplanar and form dihedral angle of 73.3°. This fact rejects any assumption that the stacking interaction between dithiole rings could explain the *cis* orientation of the molecule **4**. Nethertheless, it should be noted that the C1 ••• C1′ distance of 3.333(3) Å is somewhat shorter than the corresponding sum of van der Waals radii 3.40 Å.

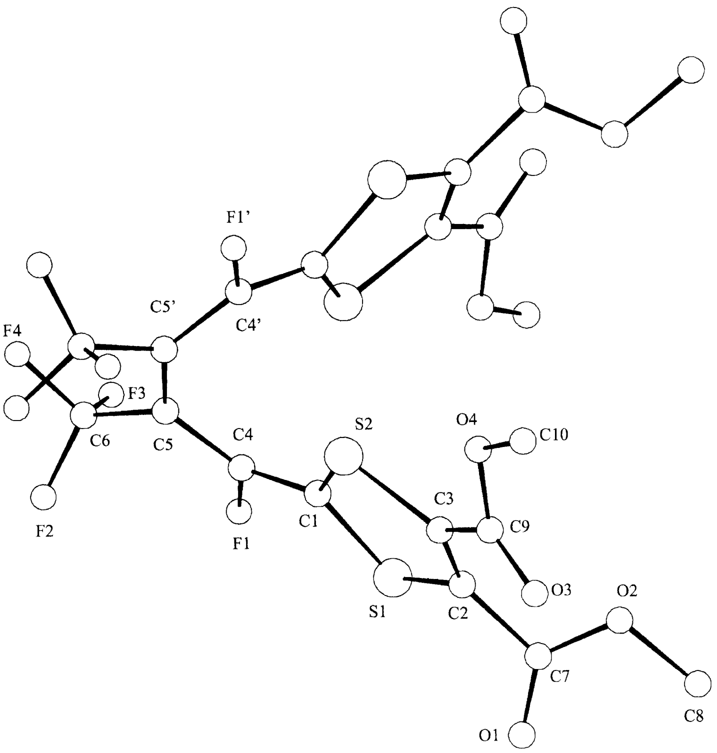
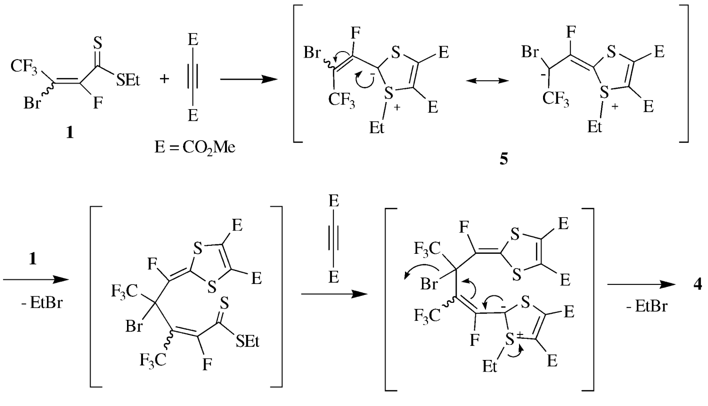


Figure 1. A perspective view and labelling scheme for the molecule **4** (primed atoms are generated from the asymmetric unit by the twofold axis); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.7442, S1–C2 1.7272, S2–C1 1.7374, S2–C3 1.7562, C1–C4 1.3673, C2–C3 1.3403, C4–C5 1.4013, C5–C5′ 1.4164; C1-S1-C2 95.51, C1-S2-C3 94.91, S1-C1-S2 115.01, S1-C2-C3 117.62, S2-C3-C2 117.02, C1-C4-C5 131.92, C4-C5-C5′ 123.02.

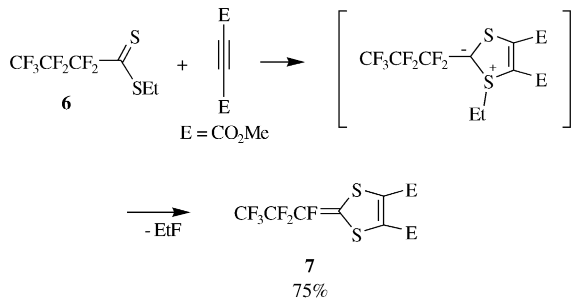
A plausible reaction pathway towards compound **4** is depicted in the Scheme 3. An initial 1,3-dipolar cycloaddition of DMAD to dithiocarboxylic moiety gives a delocalised intermediate ylide **5**, which reacts with the starting dithioester **1** as a Michael acceptor in an addition elimination process, followed by ethyl bromide elimination. A second cycloaddition followed by ethyl bromide elimination (Scheme 3) leads to **4**. Formally, **4** could be the result of a carbene coupling from debrominated **5**. This assumption seems to be ruled out, since we were not able to detect any product of trapping of such a



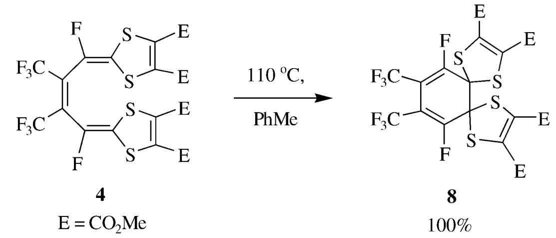
Scheme 3.

Table 1. Crystal data and structure refinement parameters for compounds **4**, **8**, and **11**.

	4	**8**	**11**
formula	$C_{20}H_{12}F_8O_8S_4$	$C_{20}H_{12}F_8O_8S_4$	$C_{14}H_6F_8O_4S_2$
a [Å]	8.971(5)	11.842(6)	8.358(3)
b [Å]	8.629(5)	33.931(11)	8.961(3)
c [Å]	17.047(6)	13.527(8)	11.979(5)
α [°]	90.0	90.0	76.68(3)
β [°]	92.20(4)	102.33(4)	81.94(3)
γ [°]	90.0	90.0	76.02(4)
V [Å^3]	1318(1)	5310(4)	843.8(8)
Z	2	8 (two independent molecules)	2
ρ_{calcd} [g cm^{-3}]	1.66	1.65	1.78
crystal system	monoclinic	monoclinic	triclinic
space group	$P2/n$	$P2_1/n$	$P\bar{1}$
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Cu_{K\alpha}$
μ [cm^{-1}]	4.42	4.39	38.25
M_r	330.3	660.5	368.4
$F(000)$	665	2661	455
crystal shape	sphere	needle	prism
crystal size [mm]	0.48 × 0.48 × 0.48	0.18 × 0.19 × 0.49	0.13 × 0.16 × 0.31
index ranges	$0 < h < 10$ $0 < k < 11$ $-21 < l < 21$	$0 < h < 13$ $0 < k < 40$ $-16 < l < 16$	$0 < h < 10$ $-8 < k < 10$ $-14 < l < 14$
θ_{max} [°]	27	26.5	70
reflections collected	2962	10866	2457
independent reflections	2593	9986	2302
reflections in refinement	2012 [$I > 3\sigma(I)$]	2798 [$I > 2.5\sigma(I)$]	1571 [$I > 3\sigma(I)$]
R(int)	0.027	0.042	0.011
parameters	181	561	307
observ./var.	11.1	5.0	5.1
R	0.037	0.079	0.042
R_w	0.039	0.076	0.044
GOF	1.084	1.188	1.190
weighting coefficients:	0.78, −0.36, 0.25, −0.35	1.45, 0.79, 1.15	1.29, 0.03, 0.91, −0.11, 0.28
largest peak/hole [e cm^{-3}]	0.40/−0.41	0.54/−0.48	0.21/−0.25



Scheme 4.



Scheme 5.

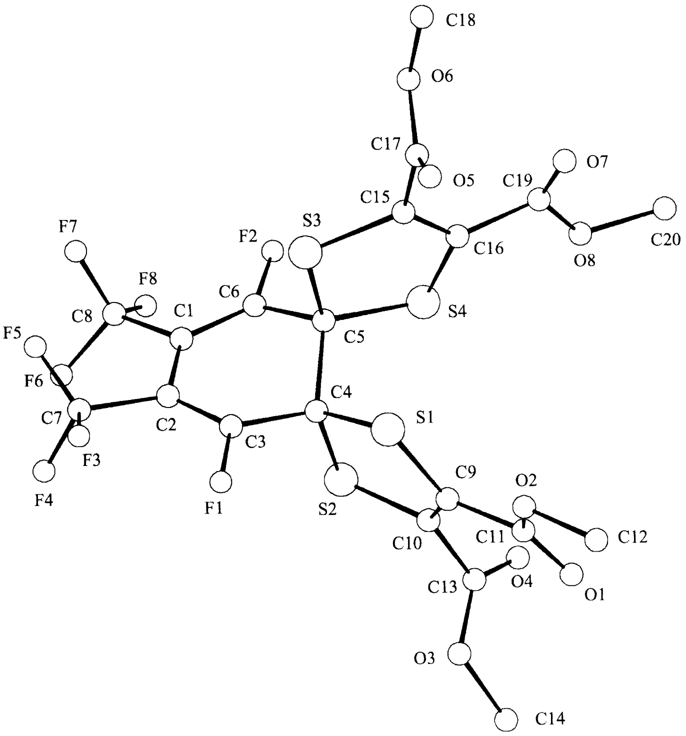


Figure 2. A perspective view and labelling scheme for the independent molecule **A** of the compound **8;** hydrogen atoms are omitted for clarity. Average for two independent molecules selected bond lengths [Å] and angles [°]: S1−C4 1.84812, S1−C9 1.75212, S2−C4 1.86511, S2−C10 1.74411, S3−C5 1.84312, S3−C15 1.73312, S4−C5 1.83512, S4−C16 1.76013, C4−C5 1.56315; C4-S1-C9 96.15, C4-S2-C10 97.15, C5-S3-C15 97.96, C5-S4-S16 96.76.

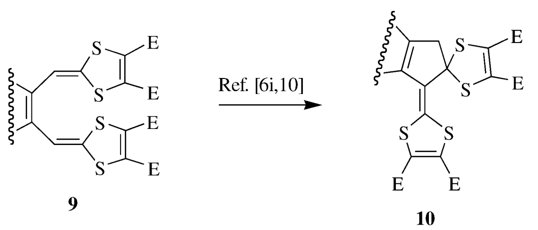
carbene when the reaction of **1** with DMAD was performed in the presence of an excess of cyclohexene.

As mentioned above, the formation of an intermediate ylide has already been observed in non-fluorinated series, with a subsequent migration of the S-alkyl group.[3] Reaction of ethyl perfluorodithiobutanoate (**6**)[9] with DMAD gave the corresponding ketene dithioacetal **7**, which evolves from a β-elimination of fluoride, preferred here to an alkyl migration (Scheme 4).

On heating in toluene for 10 minutes, compound **4** was quantitatively converted into the bis(spiro) derivative **8** (Scheme 5). The ease with which this electrocyclization occured may be explained by the structural features pointed out above.

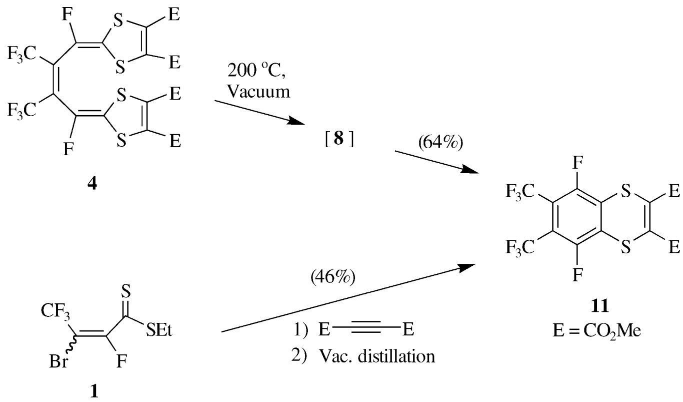
An X-ray diffraction study of **8** (Figure 2, Table 1) revealed that in solid state there are two crystallographically independent molecules **A** and **B** with virtually identical geometrical parameters. The C1–C6 ring is significantly nonplanar (e.g., the C3-C4-C5-C6 torsion angle being −47.9° in **8A** and 50.4° in **8B**) and has a halfboat conformation. The dihedral angle between dithiole rings S1-S2-C4-C9-C10 and S3-S4-C5-C15-C16 is 55.0° in the molecule **8A** and 53.0° in the molecule **8B**. The O1-O2-C11, O3-O4-C13, O5-O6-C17 and O7-O8-C19 groups are twisted out of the corresponding dithiole planes by 7.5, 77.4, 79.6 and 1.8° in the molecule **8A** and 13.2, 75.9, 78.4 and 9.6° in the molecule **8B**, respectively.

It is noteworthy that compounds with the similar but nonfluorinated structure **9** were reported to undergo an intramolecular cyclisation, in a different process induced by an acid catalyst or electrochemically; this led to the formation of the indan derivative **10** (Scheme 6).[6i, 10]



Scheme 6.

If thermolysis of compound **4** was conducted under more drastic conditions (180–200 °C, 0.01 mbar, 10 min), 5,8-difluoro-6,7-bis(trifluoromethyl)-2,3-dicarboxymethyl-1,4-benzo-dithiine (**11**) was formed in 64 % yield (Scheme 7). The reaction proceeds via compound **8**, as shown by the similar result obtained when pure **8** was thermolysed in the same conditions. It is noteworthy that the peak at *m/z* 454, which is the base peak in the mass spectra for compounds **4** and **8**, corresponds to loss of $C_6H_6O_4S_2$ fragment. Consequently, heterocycle **11** was formed in the mass spectrometer from both compounds **4** and **8**. Interestingly, the benzodithiine **11** was prepared in one step, in an overall yield of 46 % (purified product) by simply mixing **1** and DMAD at room temperature for four hours, followed by vacuum distillation (Scheme 7).



Scheme 7.

The structure of the compound **11** was identified by a single-crystal X-ray diffraction analysis (Figure 3, Table 1). The central heterocycle S1-S2-C1-C2-C3-C4 is nonplanar and folded over the S1···S2 line by 51.1°, whereas the C3–C8 benzene ring is coplanar to the S1–C4=C3–S2 bond system. The C9-O1-O2 group is coplanar, whereas the C11-O3-O4 group is orthogonal to the S1–C1=C2–S2 bond system (corresponding dihedral angles, 2.8 and 88.0°, respectively). All bond lengths and angles in molecule **11** as well as those in molecules **4** and **8** are unexceptional.[11, 12]

Compound **11** is a new representative of the fluorine-containing benzodithiines. Only few examples of compounds of this type were described in the literature.[13, 14]

Conclusion

In summary, ethyl β-bromoperfluorodithiocrotonate (**1**) reacted as a 1,3-dipole with DMAD to give an unexpected coupling product, the fluorine-containing vinylogue of tetrathiafulvalene **4**. This transformation, which combines cycloaddition and intermolecular nucleophilic substitution, is unprecedented and quite original compared to the usual synthetic ways towards the vinylogous derivatives of TTF. Compound **4** is thermally unstable and is transformed on mild heating into a product of electrocyclisation **8**, which contains two spiro 1,3-dithiole moieties. On stronger heating, the loss of one 1,3-dithiole fragment occurred forming the symmetrical polyfluoro benzodithiine **11**, which can be also obtained (yield: 46 %) directly by sequential heating and vacuum distillation of mixture of dithiocrotonate **1** and DMAD. The high interest in vinylogous derivatives of TTF and the original substitution pattern of compound **4** has prompted us to consider its optoelectronic properties, which are currently under investigation.

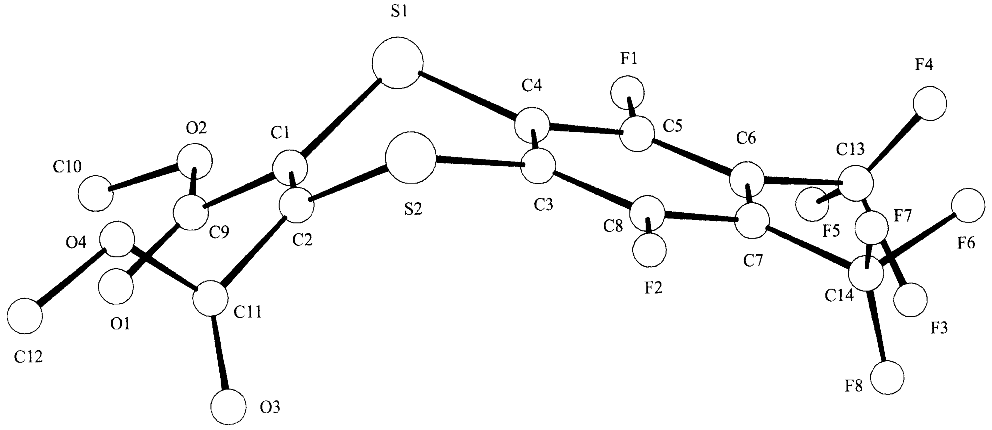


Figure 3. A perspective view and labelling scheme for the molecule **11;** hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.7694, S1–C4 1.7544, S2–C2 1.7544, S2–C3 1.7574, C1–C2 1.3206, C3–C4 1.3766; C1-S1-C4 99.52, C2-S2-C3 99.42, S1-C1-C2 121.63, S2-C2-C1 123.83, S2-C3-C4 121.63, S1-C4-C3 121.93.

Experimental Section

General remarks: Melting points are uncorrected. FTIR spectra were recorded on a MIDAC Corporation Spectrafile IR spectrometer. UV/VIS spectra were recorded on a KONTRON UVIKON 941 Plus spectrophotometer. ^{1}H, ^{13}C and ^{19}F spectra were recorded on a Bruker AC250 or AC500 spectrometer in $CDCl_3$ as the solvent. Tetramethylsilane ($\delta = 0.00$ ppm) or $CHCl_3$ ($\delta = 7.26$ ppm) were used as internal standards for ^{1}H and ^{13}C NMR spectra, and $CFCl_3$ for ^{19}F NMR spectra. MS data were obtained on a Trace MS Thermoquest apparatus (GCMS) at 70 eV in the electron impact mode. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. All reactions were monitored by GCMS. Silica gel Merck 9385 (40–63 μm) was used for flash chromatography. DMAD and solvents were obtained from commercial sources and used without further purification.

1,4-Difluoro-2,3-bis(trifluoromethyl)-but-2-ene-1,4-diylidene-2,2′-bis(4′,5′-dicarbomethoxy-1′,3′-dithiole) (4): A mixture of **1** (2.08 g, 7 mmol) and DMAD (1.99 g, 14 mmol) was stirred in the dark at room temperature for 4 h, then diluted with ethyl acetate (20 mL) and petroleum ether (35 mL); then the solution was left overnight in the refrigerator. The solvents were decanted from violet crystals, which were washed with cold petroleum ether (2×5 mL) and dried in vacuum. Yield: 1.25 g (54 %); m.p. 138–139 °C; ^{1}H NMR $\delta = 3.89$ (s, 6H; $2\,CH_3$), 3.91 ppm (s, 6H; $2\,CH_3$); ^{19}F NMR $\delta = -55.0$ (m, 3F; CF_3), -104.2 ppm (m, 1F; CF); ^{13}C NMR $\delta = 53.9$ (s, $2\,CH_3$), 54.1 (s, $2\,CH_3$), 113.5 (m, $2\,C$-CF_3), 121.4 (q, $^1J(C,F) = 278.6$ Hz, $2\,CF_3$), 125.4 (d, $^2J(C,F) = 33.9$ Hz, $2\,C$-CF), 133.5 (s, $2\,C$-C=O), 135.5 (s, $2\,C$-C=O), 139.7 (d, $^1J(C,F) = 278.6$ Hz, CF), 159.0 (s, 2 C=O), 159.4 ppm (s, 2 C=O); IR (KBr): $\tilde{\nu} = 3440, 3013, 2959, 2983, 2847, 1731$ (C=O), 1580, 1482, 1436, 1367, 1288, 1196, 1169, 1107 cm^{-1}; UV/VIS (diethyl ether): λ_{max} (ε) = 540 nm (9800); MS (70 eV, EI): m/z (%): 660 (27) [M^+], 454 (100); elemental analysis calcd (%) for $C_{20}H_{12}F_8O_8S_4$ (660.56): C 36.37, H 1.83; found: C 36.79, H 1.51.

4,5-Bis(carbomethoxy)-2-(hexafluoropropylidene)-1,3-dithiole (7): A mixture of ethyl dithioheptafluorobutyrate[9] (1.1 g, 4 mmol) and DMAD (0.57 g, 4 mmol) was stirred at room temperature for 12 h. The resulting yellow oil was purified by chromatography over silica gel (petroleum ether/dichloromethane 1:1). Compound **7** was collected at $R_f = 0.79$. Yield: 1.1 g (75 %); yellow oil; ^{1}H NMR $\delta = 3.86$ (s, 3H; CH_3), 3.87 ppm (s, 3H; CH_3); ^{19}F NMR $\delta = -84.3$ (dt, $^3J(F,F) = 6.9$, 3.4 Hz, 3F; CF_3), -118.0 (dq, $^3J(F,F) = 15.5$, 3.4 Hz, 2F; CF_2), -122.3 ppm (tq, $^3J(F,F) = 15.5$, $^4J(F,F) = 6.9$ Hz, 1F; CF); ^{13}C NMR $\delta = 53.69$ (s, CH_3), 53.71 (s, CH_3), 109.3 (tqd, $^1J(C,F) = 256.4$, $^2J(C,F) = 40.9$, $^2J(C,F) = 34.5$ Hz, CF_2), 118.4 (qtd, $^1J(C,F) = 287.7$, $^2J(C,F) = 38.6$, $^3J(C,F) = 3.7$ Hz, CF_3), 128.6 (q, $^2J(C,F) = {^3J}(C,F) = 25.7$ Hz, CS_2), 130.2 (d, $^4J(C,F) = 2.8$ Hz, C-C=O), 131.1 (dt, $^1J(C,F) = 244.0$, $^2J(C,F) = 33.5$ Hz, CF), 131.5 (t, $^4J(C,F) = {^5J}(C,F) = 3.7$ Hz, C-C=O), 159.0 (d, $^5J(C,F) = 2.3$ Hz, C=O), 159.1 ppm (s, C=O); IR (neat): $\tilde{\nu} = 2959, 1739$ (C=O), 1630 (C=C), 1581 (C=C), 1436, 1263, 1214, 1156, 1123, 1094 cm^{-1}; MS (70 eV, EI): m/z (%): 368 (90) [M^+], 337 (51) [$M^+ - OCH_3$], 299 (100) [$M^+ - CF_3$]; elemental analysis calcd (%) for $C_{10}H_6F_6O_4S_2$ (368.28): C 32.61, H 1.64; found: C 32.46, H 1.56.

11,14-Difluoro-2,3,8,9-tetra(carbomethoxy)-12,13-bis(trifluoromethyl)-1,4,7,10-tetrathiadispiro[4.0.4.4]tetradeca-2,8,11,13-tetraene (8): A solution of compound **4** (110 mg, 0.166 mmol) in toluene (3 mL) was refluxed for 10 min. The solvent was evaporated in vacuum to give compound **8** in quantitative yield. After recrystallisation from petroleum ether, 95 mg (86 %) of yellow crystals were obtained. M.p. 108–109 °C; ^{1}H NMR $\delta = 3.84$ ppm (s, $4\,CH_3$); ^{19}F NMR $\delta = -57.8$ (m, 3F, CF_3), -83.8 ppm (m, 1F, CF); ^{13}C NMR $\delta = 53.6$ (s, $4\,CH_3$), 78.6 (d, $^2J(C,F) = 18.4$ Hz, $C_{quaternary}$), 105.8 (m, $2\,C$-CF_3), 120.0 (q, $^1J(C,F) = 280.4$ Hz, $2\,CF_3$), 128.4 (m, C-CF, C-C=O), 157.6 (d, $^1J(C,F) = 297.8$ Hz, 2 CF), 158.9 ppm (s, 4 C=O); IR (KBr): $\tilde{\nu} = 2960, 1731$ (C=O), 1667, 1624, 1596, 1435, 1371, 1343, 1259, 1224, 1162 cm^{-1}; MS (70 eV, EI): m/z (%): 660 (11) [M^+], 454 (100); elemental analysis calcd (%) for $C_{20}H_{12}F_8O_8S_4$ (660.56): C 36.37, H 1.83; found: C 36.74, H 1.76.

5,8-Difluoro-6,7-bis(trifluoromethyl)-2,3-bis(carboxymethyl)-1,4-benzodithiine (11): DMAD (1.64 g, 11.6 mmol) was added to dithiocarboxylate **1** (1.72 g, 5.8 mmol), and the resulting mixture was stirred for 4 h at 25 °C. The crude mixture was distilled in vacuum (b.p. 62–70 °C, 0.02 mbar) to give the corresponding dithiine **11** as red liquid. Compound **11** was additionally purified by column chromatography on silica gel (petroleum ether/ethyl acetate 87:13) and recrystallised from petroleum ether. Yield: 0.6 g (46 %); yellow crystals; m.p. 110–111 °C; ^{1}H NMR $\delta = 3.88$ ppm (s, $2\,CH_3$); ^{19}F NMR $\delta = -55.0$ (m, 3F; CF_3), -107.5 ppm (m, 1F; CF); ^{13}C NMR $\delta = 53.9$ (s, CH_3), 117.3 (m, C-CF_3), 120.8 (qd, $^1J(C,F) = 279.7$, $^3J(C,F) = 2.3$ Hz, CF_3), 129.9 (d, $^2J(C,F) = 24.8$ Hz, C-CF), 133.3 (s, C-C=O), 152.5 (d, $^1J(C,F) = 259.2$ Hz, CF), 161.6 ppm (s, C=O); IR (KBr): $\tilde{\nu} = 2964, 1747$ (C=O), 1560, 1422 cm^{-1}; MS (70 eV, EI): m/z (%): 454 [M^+], 423, 365, 324 (100); elemental analysis calcd (%) for $C_{14}H_6F_8O_4S_2$ (454.32): C 37.01, H 1.33; found: C 36.89, H 1.12.

Thermolysis of 4 to 11: Compound **4** (132 mg, 0.2 mmol) was heated for 3 min in Kugelrohr apparatus at 200 °C and then vacuum (0.01 mbar) was carefully connected. Volatile product was collected and filtered through short column with silica gel by using a mixture of petroleum ether/ethyl acetate (80:20) as eluent. Yield of **11**: 58 mg (64 %).

X-ray crystal structure determination of compounds 4, 8 and 11: Crystal data, data collection and processing parameters are given in Table 1. All crystallographic measurements were performed at 20 °C on a CAD-4-Enraf-Nonius diffractometer using ω-2θ scan mode (the ratio of the scanning rates $\omega/2\theta = 1.2$). All data were corrected for Lorentz and polarization effects and an empirical absorption correction based on azimuthal scan data[15] was applied. The structures were solved by direct methods. Non-hydrogen atoms were refined by full-matrix least-squares technique in the anisotropic approximation (in **8** the terminal C(O)OMe groups were refined isotropically). In **4** and **11** all hydrogen atoms were located in the difference Fourier maps and included in the final refinement with the fixed positional and thermal parameters. In **8** hydrogen atoms were placed in calculated positions and included in refinement with fixed positional and thermal parameters. The Chebushev weighting scheme[16] was used. All structural calculations were carried out by using the CRYSTALS program package.[17]

CCDC-182939 (**4**), CCDC-197227 (**8**), and CCDC-158751 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the CNRS for temporary positions (Yu.G.S. and V.M.T.). H. Baillia and S. Lanthony are thanked for NMR spectra and microanalyses.

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Received: February 11, 2003 [F4839]