Table I. NMR Spectra of (−)-Camphanic Acid Esters of the Indicated Alcohols. All Spectra Were Recorded at 100 MHz as CCl$_4$ Solutions in the Presence of 30 mol % Eu(dpm)$_3$

Esters of	^{1}H$_R$^{a}	^{1}H$_S$^{a}
2-Phenylethanol		
a, (1*RS*) [1-^{2}H$_1$]	5.2 (t, *J* = 6 Hz)	5.4 (t, *J* = 6 Hz)
b, (1*S*) [1-^{2}H]	5.2 (t, *J* = 6 Hz)	ND
c, (1*R*) [1-^{2}H$_1$]	ND^b	5.4 (t, *J* = 6 Hz)
Benzyl alcohol		
a, (1*RS*) [1-^{2}H$_1$]	5.70 (s)	5.88 (s)
b, (1*S*) [1-^{2}H$_1$]	5.70 (s)	ND
c, (1*R*) [1-^{2}H$_1$]	ND	5.88 (s)

^{a} Chemical shifts of the enantiotopic hydrogens (in ppm). ^{b} ND, not detectable..

oxidation of the (1*S*)-octanol **4b** to octanal **1c** proceeded with the complete retention of tritium, while the oxidation of the (1*R*)-octanol **5b** to octanal **1a** involved the loss of 98% tritium.

To test the generality of the inversion procedure, (1*S*)-[1-^{2}H$_1$]-2-phenylethanol (**8a**) and (1*S*)[1-^{2}H$_1$]-benzyl alcohol (**8b**) were prepared by HLAD–NAD reduction of the corresponding [1-^{2}H] aldehydes. The (1*S*) alcohols were treated with $(C_6H_5)_3P/C_6H_5CO_2H/EtO_2CN{=}NCO_2Et/THF$, as described above. The resulting (1*R*) benzoates were saponified (methanolic KOH) to give (1*R*)[1-^{2}H$_1$]-phenylethanol (**9a**) and (1*R*)[1-^{2}H$_1$]-benzyl alcohol (**9b**) in good yield. The 100-MHz Eu(dpm)$_3$ analyses of the (−)-camphanic acid esters of alcohols **9a** and **9b** indicated the presence of at least 95% excess (1*R*) alcohols in each case (see Table I).

The described procedure represents a facile synthesis of primary (1*R*) alcohols from the more accessible (1*S*) alcohols. In the systems investigated, the reaction proceeds in high yield with complete inversion of configuration. Aldehydes with a high C-1 tritium content can be prepared by quenching the anion derived from **2a** with tritiated water of high specific activity. It follows that by using the described methods, (1*S*) and (1*R*) [1-^{3}H] alcohols and the chiral methyls derived from these alcohols will have a high specific activity of tritium.

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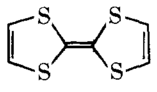
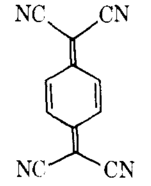
Unsymmetrical Dimethyltetrathiafulvalene[1]

Summary: A hitherto unknown unsymmetrically substituted tetrathiafulvalene (substitution on only one ring) was prepared, isolated, and purified, and its spectroscopic and physical properties are described and compared with those of other members of the family; the title compound forms highly conducting salts with TCNQ and other anions.

Sir: Organic materials whose electrical conductivity in the solid state increases with decreasing temperature belong to the theoretically interesting family of "low dimensional" or "one dimensional metals". Members of this class of substances have in common the peculiar property whereby the molecular charge carriers stack uniformly along a given axis. The solid-state packing arrangement of all known members of this family (whether organic or inorganic) consists of independent, uniform stacks of donors and/or acceptors and are subject to a theoretically predicted solid-phase transition[2a] which eventually converts them to insulators (usually at temperatures below 200 K). Within this class the most highly conducting organic materials are based on TTF (**1**) and TCNQ (**2**).

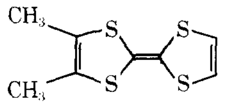


TTF (1)



TCNQ (2)

While an unsymmetrically substituted TCNQ derivative (monomethyl TCNQ), has been prepared and its electrical properties in combination with TTF have been studied,[2b] no such simple unsymmetrical TTF compounds are known. The only previously known asymmetrical TTF compound is the monomethyl dibenzotetrathiafulvalene,[3] a material which does not yield organic metals.[3] This paper is a report on the synthesis, separation, purification, and comparative spectroscopic properties of various potentially interesting methylated TTF molecules, especially the title compound (UDMTTF, **3**). The physical measurements and preparation of organic conductors based on these donors will be reported separately.



UDMTTF (3)

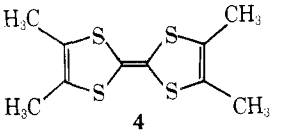
Because monomethyl TTF was expected to have very similar properties to TTF and dimethyl TTF, its synthesis in

Table I

Compd	Mp, °C (corr)	λ_{max} (ϵ),[a] nm	NMR, τ	IR (KBr), cm^{-1}	EPR (propylene carbonate)[b]
TTF (**1**), orange-yellow needles	119.1–119.3	303 (12 800), 316 (11 400), 368 (2 000), 450 (230)	3.75 (s) [CCl_4 (TMS)]	1530 (w), 1250 (w), 1075 (w), 870 (w), 797 (m), 782 (m), 734 (m)	Quintet (CH_3CN) $g = 2.00838$ $a_H = 1.26$ G
UDMTFF (**3**), orange-yellow needles	117.3–118.8	278 (sh) (10 200), 290 (sh) (12 700), 299 (14 300), 308 (sh) (13 500), 322 (sh) (12 300), 360 (sh) (3 070), 445 (640)	8.08 (s, 6 H), 3.78 (s, 2 H) [CS_2 (TMS)]	2900 (w), 1420 (m), 1180 (w), 1080 (m), 797 (m), 778 (m), 733 (m)	Seventeen lines $g = 2.0078$ $a_H \simeq 1.18$ G $a_{CH_3} \simeq 0.82$ G
SDMTTF (**5**), orange-yellow needles	109–111	278 (sh) (12 300), 290 (sh) (14 800), 298 (15 800), 308 (14 800), 321 (13 500), 355 (sh) (4 960), 440 (sh) (1 340)	7.95 (d, 6H), 4.18 (q, 2H, $J = 1.5$ Hz) [$CDCl_3$ (TMS)]	1630 (w), 1480 (w), 1420 (m), 1220 (m), 1110 (s), 1030 (w), 808 (s), 775 (s), 748 (s)	Eleven lines $g = 2.0079$ $g_{CH_3} \simeq 0.64$ G $a_H \simeq 1.28$ G
TMTTF (**4**), salmon-colored needles	240.5–241.3	287 (sh) (12 000), 297 (sh) (13 000), 315 (14 000), 327 (13 800), 473 (248)[c]	8.13 (s) [CS_2 (TMS)]	2900 (w), 1630 (w), 1420 (m), 1180 (m), 1085 (m), 782 (s)	Thirteen lines $g = 2.0077$ $a_{CH_3} \simeq 0.74$ G

[a] In hexane. [b] As fluoroborate salt. [c] In 1,2-dichloroethane.

a manner analogous to reaction 1 was not attempted. On the other hand, we expected **3** to be different enough from TTF and TMTTF [tetramethyl TTF (**4**)][4] so that its separation from the latter would be viable.



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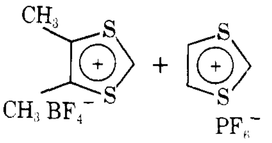
The title compound was prepared by the straightforward approach[4b,5] shown in eq 1.



$$\xrightarrow[CH_3CN]{(C_2H_5)_3N} \tfrac{1}{3}\text{TTF} + \tfrac{1}{3}\text{UDMTTF} + \tfrac{1}{3}\text{TMTTF} \quad (1)$$

The products TTF and TMTTF are soluble and insoluble (respectively) in cold acetonitrile. Thus, **3** crystallized from a slowly cooling solution of the acetonitrile washings of the crude reaction mixture. Reaction 1 afforded 59% isolated yield of TMTTF and 78% isolated yield of thrice recrystallized **3** (based on a theoretically possible yield of 33% for each component).

Compound **3** is a yellow crystalline solid: mp 117.2–118.5 °C (cf. 119 °C for TTF and 241 °C for TMTTF); mass spectrum (*m/e*) 232 (parent, plus five isotope peaks in proper ratio), 187, 130 (dimethyldithiolium carbene), 102 (base peak, dithiolium carbene), 76 (CS_2), 54 (dimethylacetylene). There were no peaks at 260 or 204, proving conclusively the absence of contamination by TTF or TMTTF. Interestingly, the dimethyldithiolium species is less stable than the unsubstituted dithiolium based on the relative abundance of the *m/e* 130 vs. the *m/e* 54) and fragments of CS_2 and dimethylacetylene.

The electronic spectra of **1**, **3**, and **4** are presented in Table I. Because **3** is the most unsymmetric it exhibits the largest differences as compared to **1** and **4**.

Figure 1 shows the electron spin resonance spectrum of UDMTTF$^+$. The spectrum consists of seventeen lines resulting from the overlap of the lines from two types of H hyperfine couplings.

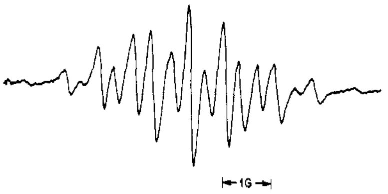
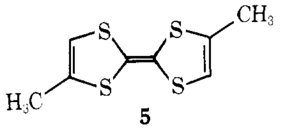


Figure 1. Electron spin resonance spectrum of UDMTTF$(BF_4)_{0.45}$ in propylene carbonate: $g = 2.0078$, $a_H \simeq 1.1$ G, $a_{CH_3} \simeq 0.8$ G.

For comparison, symmetrical dimethyl TTF (SDMTTF, **5**, misnomered ATTF by others) was prepared in a similar manner from 4-methyl-1,3-dithiolium fluoroborate and triethylamine. Although two possible isomers are expected (cis and trans), we believe that the isolated material, because of its physical characteristics (lower solubility in acetonitrile, melting point), must be the *trans*-SDMTTF. Previous workers have apparently not been successful in separating the isomers of the SDMTTF.[6] The compound which we isolated exhibits the properties shown in Table I.



5

As was foreseen, **3** forms highly conducting salts with TCNQ and other anions as does TTF itself.[7] We are currently studying the single-crystal physical properties of its salts and "stereo alloys" of it with unsubstituted and fully methylated TTF.

The experimental procedure[8] follows. To a cooled (0 °C), magnetically stirred solution of 4,5-dimethyl-1,3-dithiolium fluoroborate (1.97 g, 9.04 mmol) and 1,3-dithiolium fluoroborate (or hexafluorophosphate) (1.70 g, 9.04 mmol) in a minimum amount of dry acetonitrile (~15 ml) was added triethylamine, dropwise, until the formation of orange-yellow crystals was obvious (~1.0 g, 10 mmol). After stirring for an additional 10 min, the mixture was poured into 300 ml of water and extracted with cyclohexane (6 × 100 ml). The combined organic layers were washed with water (2 × 100 ml), dried over sodium sulfate, filtered, and then concentrated to dryness under reduced pressure. The resulting yellowish red solid was washed with ice-cold acetonitrile ($\sim$250 ml) to remove TTF and UDMTTF. Recrystallization of the remaining solid from acetonitrile afforded 0.46 g (59%) of tetramethyl TTF.

The acetonitrile washings from above were concentrated to dryness and the resulting solid taken up in a minimum of boiling acetonitrile. Fractional crystallization from this solution afforded several crops of UDMTTF crystals. Two recrystallizations of these combined drops from acetonitrile (Norit, filtration through acid-washed Celite) gave 0.545 g (78% yield) of orange-yellow crystals (mp 117.3–118.5 °C corr). See Table I for additional data.

Acknowledgment. The authors thank Dr. D. J. Freed for performing the mass spectroscopic analyses of some of these compounds.

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