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The Synthesis of Primary, Secondary and Tertiary Aminomethyltetrathiafulvalenes

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Key Words: tetrathiafulvalenyllithium; formyltetrathiafulvalene; imines; amino derivatives; organic conductors.

***Abstract**: The title compounds have been prepared in one or two steps, using either formyltetrathiafulvalene or tetrathiafulvalenyllithium as starting materials.*

INTRODUCTION

The tetrathiafulvalene skeleton remains one of the most promising in the field of organic conductors and superconductors [1], in addition to some conjugated polymers [1c] and the recently discovered doped fullerenes [2], whose chemistry is still in its infancy.

Although many tetrachalcogenofulvalene derivatives are known [3], most of them contain either electron-withdrawing groups (and are consequently of little interest as organic conductors because the radical cation will form only at a high oxidation potential) or bear alkyl, aryl or other groups that show poor reactivity, such as ethers (BEDO-TTF [4]) or thioethers (*e.g.* BEDT-TTF [3d,5] and MDT-TTF [6]). No doubt, this has restricted the use of many standard transformations that could give rise to a wealth of new donors.

Since the introduction of heteroatoms on the periphery of the parent system is known to increase the dimensionality of the desired materials, tetrathiafulvalenes containing other heteroatoms, such as halogens [7], phosphorus [8] and silicon [9] have recently been synthesized, although there are still very few reports regarding their chemistry [9b] and derived materials.

With regard to nitrogen-bearing tetrathiafulvalenes, some fused systems containing pyridine [10], pyrazine[10], pyridazine [11] and pyrrole [12] rings have been prepared, but there are very few examples of tetrathiafulvalenes with amino groups [13,14]. This is unfortunate for two reasons:

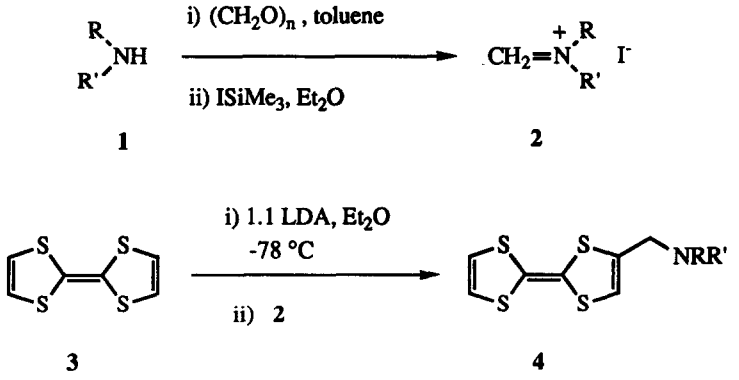
- As far as their chemistry is concerned, the introduction of sp^3 nitrogen atoms should give greater synthetic flexibility than that caused by the presence of ethers and their analogues, thus allowing easier entry to new derivatives, including molecules with two or more tetrathiafulvalene rings [15], and

- With regard to the new materials, they will hopefully show not only enhanced dimensionality, but also promising features such as intercalants, candidates for forming Langmuir-Blodgett films [1a] (because of the easy introduction of long alkyl chains) and, in the case of the primary and secondary derivatives, the existence of hydrogen bonding [16], an interaction of great interest in crystal engineering and κ-phase design.

A preliminary report on the synthesis of *N,N*-disubstituted aminomethyltetrathiafulvalenes has recently appeared [14] and, as a continuation of this work, we herein describe in full the preparation of these derivatives **4**, as well as the first synthesis of secondary and primary aminomethyltetrathiafulvalenes, **8** and **9** respectively.

RESULTS AND DISCUSSION

Tertiary derivatives **4** have been prepared according to Scheme 1:



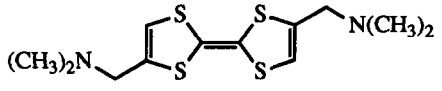
1 **2** **3** **4**

a R = R'= CH_3
b R-R' = $(CH_2)_5$
c R = CH_3, R'= CH_2Ph

Scheme 1

This approach seemed attractive since the reaction of organolithium or Grignard reagents with Eschenmoser's salts is not without precedent in the literature [17] and tetrathiafulvalenyllithium is easily generated[16a]. In our experience, the most suitable method for the synthesis of compounds **2** consisted in the cleavage [18] of formaldehyde aminals with iodotrimethylsilane. The starting products were prepared from secondary amines **1** and paraformaldehyde, using the previously described procedure [19]. Both steps proceed in nearly quantitative yield. The hygroscopic Eschenmoser's salts **2** thus prepared were used immediately without further purification and added over the suspension of tetrathiafulvalenyllithium in Et_2O. The reaction gives, after column chromatography, pure compounds **4** as yellow oils which solidify when left in the refrigerator. Yields range from 35 to 44%.

Not unexpectedly [16a], a very small amount of a disubstituted tetrathiafulvalene was isolated in one run to obtain **4a**.



5 (*Z*) + (*E*)

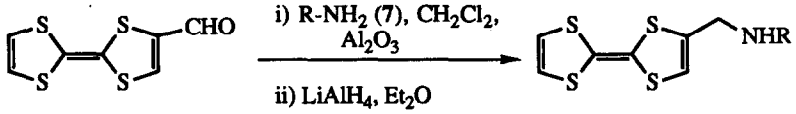
We have assigned structure **5**, namely 4,4'(5')-bis(dimethylaminomethyl)tetrathiafulvalene, to this compound on the basis of its ^{1}H-NMR spectrum, which shows one signal at δ 6.04, characteristic of a TTF ring proton adjacent to an *N,N*-disubstituted aminomethyl group. The alternative structure (a 4,5-disubstituted

TTF) can be ruled out, since it should show a singlet around δ 6.27, which was not observed.

The scope of these aminomethylation reactions can, in principle, be extended to the synthesis of primary amines by the use of *N,N*-bis(trimethylsilyl) derivatives [20], which formally act as a source of $^{+}CH_2NH_2$. Nevertheless, the reaction of *N,N*-bis(trimethylsilyl)ethoxymethylamine (previously treated with halotrimethylsilanes [21,22] or not) with TTF-Li did not afford the desired compounds, starting product **3** being recovered in good yield.

Thus, a different approach was sought for the synthesis of aminomethyltetrathiafulvalenes bearing one or two N-H bonds.At first sight, a possible entry to these compounds would be the reduction of tetrathiafulvalenecarboxamides and nitriles, but it is known that the reduction of tetrathiafulvalenecarboxylic acid derivatives occurs to a small extent (if at all) [16d, 16e, 23]. In our experience these previous observations were confirmed, since all atempts to reduce tetrathiafulvalenecarboxamides have so far proved unsuccessful. Nevertheless, the easy reduction of tetraformyltetrathiafulvalene and tetraformyltetraselenafulvalene to the corresponding tetrakis(hydroxymethyl) derivatives[16e] led us to suppose that treatment of formyltetrathiafulvalene-derived imines could yield the corresponding secondary amines **8** upon reduction.

This is in fact the case, and the adopted synthetic route is depicted in Scheme 2.



6 **8**

a R = Bu
b R = CH_2Ph
c R = 4-Me-C_6H_4
d R = *n*-$C_{18}H_{37}$

Scheme 2

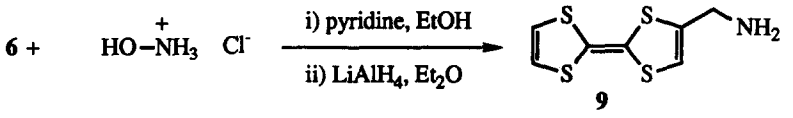
The reaction of formyltetrathiafulvalene **6** [16a] with aliphatic and aromatic amines **7** proceeds in refluxing dichloromethane and in the presence of dehydrating agents to give the corresponding imines. When anhydrous $MgSO_4$ was used, very poor results were obtained. Molecular sieves (4 Å) were more efficient, but the use of neutral activated grade I alumina results in shorter reaction times and a simpler work-up. The colour of the reaction mixture changes from deep red to orange and when all the aldehyde has disappeared (TLC) the solvent is evaporated under vacuum. The corresponding imines are not isolated, due to their instability, but are reduced *in situ* with $LiAlH_4$ in Et_2O. The reduction proceeds smoothly at room temperature, the colour of the mixture changing from orange to yellow. It is worth mentioning that $NaBH_4$ is incapable of carrying out the reduction. Compounds **8** are yellow solids (except for **8a**, which is an oil) which slowly darkens when left.

Compound **8** (R = CH_3) could not be obtained, since the use of gaseous methylamine only led to a complex mixture. Attempted hydrogenolysis of the benzyl group of **4c** (H_2 1 atm, 10% palladium on charcoal, EtOH, room temperature) also failed, compound **4c** being recovered unchanged.

Primary amine **9** seemed an especially interesting target, for the reasons previously discussed. Taking into account the successful approach to amino derivatives **8**, we thought that the reduction of oximes or oxime

ethers derived from formyltetrathiafulvalene **6** might yield the desired compound **9**. Thus, the reactions of **6** with methoxyamine or hydroxylamine hydrochlorides in pyridine/EtOH gave the corresponding oximes **10a** and **10b** respectively, along with small amounts of unidentified byproducts (as revealed by NMR), that could not be eliminated even after column chromatography.

Subsequent reduction attempts were carried out with the crude oximes, using either diborane [24] or $LiAlH_4$. The results with the former, using THF as a solvent, were disappointing since no reaction was observed after refluxing the mixture for several hours. On the other hand, $LiAlH_4$ did reduce both oximes, the most successful results being obtained with formyltetrathiafulvalene oxime **10b** (Scheme 3):



9

Scheme 3

In fact, when the crude oxime was dissolved in Et_2O and treated with $LiAlH_4$, pure compound **9** was obtained as a yellow oil after column chromatography. It was quickly characterised after isolation, since **9** decomposes in a few hours when left.

Cyclic voltammetry of new donors **4**, **8** and **9** (experimental conditions: donor (*ca.* 5 x 10^{-4} M), electrolyte $Bu_4N^+PF_6^-$ (*ca.* 1 x 10^{-1} M) in dry acetonitrile, at 20°C, *vs.* SCE, Pt working and counter electrodes, scan rate 200 mV.s^{-1}) show two reversible oxidation peaks at 0.29 - 0.32 V ($E_1^{1/2}$) and 0.67 - 0.70 V ($E_2^{1/2}$), similar to those of TTF itself (**3**): $E_1^{1/2}$ = 0.32, $E_2^{1/2}$ = 0.72. In fact, the ability of some of these donors to form conducting charge-transfer compounds with TCNQ has already been reported [14].

CONCLUSIONS

In conclusion, in this paper we report the first synthesis of a complete series of aminomethyltetrathiafulvalenes bearing primary, secondary and tertiary amino groups. All the compounds were prepared in one or two steps using either formyltetrathiafulvalene (easily prepared from TTF-Li) or tetrathiafulvalene itself as starting materials. Thus, the advantages of the lithiation methodology in the preparation of unsymmetrical TTF derivatives are again clearly demonstrated, since no multistep syntheses and tedious separations of intermediates are required.

Furthermore, the introduction of sp^3 nitrogen atoms in the side chain of the TTF will no doubt increase the number of new derivatives, through the use of current synthetic manipulations. Especially interesting in this respect are those compounds bearing N-H bonds which additionally offer new possibilities of studying the influence of hydrogen-bonding in the crystal packing of their radical-cation salts. Unfortunately, this kind of study would be severely limited in the case of the *a priori* interesting donor **9**, because of its low stability.

The synthesis and properties of charge-transfer compounds and radical-cation salts of these new donors will be described in due course.

EXPERIMENTAL

Melting points were determined using a Büchi 510 apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-

NMR spectra were run on a Varian 300 Unity spectrometer using $CDCl_3$ as a solvent. Mass spectra were obtained with a VG Autospec spectrometer using EI (70 eV), LSIMS (Cs^+ ions, *m*-nitrobenzyl alcohol as a matrix) or CI (methane) as ionization techniques. Cyclic voltammetry measurements were carried out on a Princeton Applied Research 273 potentiostat-galvanostat. Column chromatography was performed on silica gel (70 - 230 mesh). Tetrathiafulvalene was purchased from Aldrich and used without further purification.

N,N-dialkyl(methylene)ammonium iodides **2**: *General Procedure*

To a stirred solution of the corresponding secondary amine **1** (60 mmol) in anhydrous toluene (40 mL), paraformaldehyde (0.9 g, 30 mmol) is added portionwise at room temperature and the mixture is refluxed with azeotropic removal of water via a Dean and Stark trap. After 4 hours the toluene is vacuum distilled, thus yielding the crude aminal, which is purified by distillation and isolated as a colourless liquid. Yields range from 80 to 90%. These aminals are used for the preparation of the desired Eschenmoser's salts.

NOTE: The following operations are carried out in a flame-dried system, repeatedly evacuated and purged with nitrogen, because of the hygroscopicity of compounds **2**: To a stirred solution of trimethylsilyl iodide (2.0 g, 10 mmol) in anhydrous Et_2O (10 mL), a solution of the corresponding aminal (10 mmol) in Et_2O (15 mL) is added dropwise at room temperature. A white precipitate is formed and the mixture is stirred for 30 minutes. The resulting solid is vacuum-filtered, washed with anhydrous Et_2O (3 x 20 mL) and used immediately without further purification. Yields are nearly quantitative.

N,N-disubstituted aminomethyltetrathiafulvalenes **4**: *General Procedure*

To a stirred solution of LDA (5.5 mmol), freshly prepared from diisopropylamine (0.555 g, 5.5 mmol) and *n*-BuLi (1.6 M in hexanes, 3.5 mL), in dry Et_2O (50 mL) at -78 °C under dry nitrogen, is added commercial TTF **3** (1.020 g, 5 mmol). After 45 - 60 min., the corresponding *N,N*-disubstituted methyleneammonium iodide **2** (7.5 mmol) is added to the lemon-yellow suspension. The reaction mixture is kept at -78 °C for 2.5 h. and then allowed to warm to room temperature overnight. Water (25 mL) is added to the crude mixture and the ethereal layer is separated, dried ($MgSO_4$) and evaporated *in vacuo* to afford crude compound **4**, which is purified on a silica column (eluent hexane-ether 4:1).

N,N-Dimethylaminomethyltetrathiafulvalene **4a**: Yield (%): 44. M.p.(°C): 78-80. ^{1}H-NMR δ: 2.24 (6H, s, CH_3), 3.17 (2H, d, J = 1.1 Hz, CH_2), 6.08 (1H, t, J = 1.1 Hz, =CH), 6.27 (2H, s, =CH). ^{13}C-NMR δ: 45.0, 59.4, 110.0, 110.2, 114.1, 118.8, 119.1, 136.4. EI MS m/z(%): 261 (M^+, 27), 204 (18), 146 (9), 58 (100). Anal. Calcd. for $C_9H_{11}NS_4$: C, 41.35; H, 4.24; N, 5.36. Found: C, 41.48; H, 4.12; N, 5.54. C.V.: $E_1^{1/2} = 0.30$, $E_2^{1/2} = 0.69$.

N,N-Pentamethyleneaminomethyltetrathiafulvalene **4b**: Yield (%): 38. M.p.(°C): 110-112. ^{1}H-NMR δ: 1.40 - 1.43 (2H, m, CH_2), 1.53 - 1.61 (4H, m, CH_2), 2.35 - 2.45 (4H, m, CH_2), 3.23 (2H, d, J = 1.2 Hz, TTF-CH_2), 6.10 (1H, t, J = 1.2 Hz, =CH), 6.27 (2H, s, =CH). ^{13}C-NMR δ: 24.0, 25.6, 54.1, 58.6, 109.7, 110.6, 114.2, 118.9, 119.1, 136.1. EI MS m/z(%): 301 (M^+, 12), 218 (7), 146 (15), 98 (100). Anal. Calcd. for $C_{12}H_{15}NS_4$: C, 47.81; H, 5.01; N, 4.65. Found: C, 47.76; H, 5.12; N, 4.46. C.V.: $E_1^{1/2} = 0.30$, $E_2^{1/2} = 0.68$.

N-methyl-N-benzylaminomethyltetrathiafulvalene **4c**: Yield (%): 35. M.p.(°C): 68-70. ^{1}H-NMR δ: 2.20 (3H, s, CH_3), 3.28 (2H, d, J = 1.3 Hz, TTF-CH_2), 3.51 (2H, s, CH_2-Ar), 6.09 (1H, t, J = 1.3 Hz, =CH), 6.31 (2H, s, =CH), 7.24 - 7.32 (5H, m, Ar-H). ^{13}C-NMR δ: 42.0, 57.2, 61.2, 109.9, 110.6, 113.8, 118.9, 119.1, 127.1, 128.3, 128.9, 137.1, 138.3. EI MS m/z(%): 337 (M^+, 4), 146 (12), 134 (26), 91 (100).CI MS m/z(%): 338 (M+ 1, 100), 217 (29). Anal. Calcd. for $C_{15}H_{15}NS_4$: C, 53.38; H, 4.48; N, 4.15. Found: C, 53.24; H, 4.37; N, 3.98. C.V.: $E_1^{1/2} = 0.29$, $E_2^{1/2} = 0.67$.

4,4'(5')-bis(dimethylaminomethyl)tetrathiafulvalene **5**: ^{1}H-NMR δ: 2.22 (6H, s, CH_3), 3.15 (2H, s, CH_2), 6.04 (1H, s, =CH). EI MS, m/z: 318 (M^+).

N-substituted aminomethyltetrathiafulvalenes **8**: *General Procedure*

To a stirred solution of formyltetrathiafulvalene **6** [16a] (0.232 g, 1 mmol) in dichloromethane (15 mL),

neutral activated grade I alumina (0.5 g) and the corresponding amine **7** (1.2 mmol) are sequentially added. The mixture is refluxed under nitrogen until aldehyde **6** has completely reacted, as judged by TLC (usually 8 - 10 hours). The alumina is filtered off and the filtrate is evaporated under vacuum. The resulting oil is dissolved in dry Et_2O (15 mL), lithium aluminium hydride (0.019 g, 0.5 mmol) is added and the mixture is stirred at room temperature for 4 - 5 hours. Ethyl acetate (40 mL) and then a few drops of water are added to destroy excess hydride and the resulting mixture is filtered. The organic solution is evaporated and crude product **8** is purified on a silica column, first eluted with hexane - ether 3:7 and then with ether - methanol 15:1. (For **8c** the only elution is carried out with hexane - ether 7:3). Pure products **8** are isolated as yellow oils.

N-butylaminomethyltetrathiafulvalene **8a**: Yield (%): 20. M.p.(°C): oil.^{1}H-NMR δ: 0.89 (3H, t, J = 7.1 Hz,CH_3), 1.28 - 1.35 (2H, m, CH_2), 1.40 - 1.46 (2H, m, CH_2), 1.64 (1H, br s, NH), 2.58 (2H, t, J = 7.0 Hz, N-CH_2), 3.54 (2H, d, J = 1.3 Hz, TTF-CH_2), 6.07 (1H, t, J = 1.3 Hz, =CH), 6.27 (2H, s, =CH). ^{13}C-NMR δ: 13.9, 20.3, 32.0, 48.6, 49.4, 113.4, 118.9, 119.1, 137.5. EI MS m/z(%): 289 (M^+, 33), 217 (10), 204 (100), 146 (70), 114 (42), 102 (41).Anal. Calcd. for $C_{11}H_{15}NS_4$: C, 45.64; H, 5.22; N, 4.84. Found: C, 45.83; H, 5.05; N, 4.99. C.V.: $E_1^{1/2}$ = 0.29, $E_2^{1/2}$ = 0.68.

N-benzylaminomethyltetrathiafulvalene **8b**: Yield (%): 35. M.p.(°C): 62-64.^{1}H-NMR δ: 1.83 (1H, br s, NH), 3.54 (2H, s, TTF-CH_2), 3.78 (2H, s, CH_2-Ar), 6.08 (1H, s, =CH), 6.27 (2H, s, =CH), 7.25 - 7.35 (5H, m, Ar-H). ^{13}C-NMR δ: 48.1, 52.2, 110.0, 110.4, 114.3, 118.9, 119.1, 127.2, 128.2, 128.4, 136.5, 139.0. EI MS m/z(%): 323 (M^+, 14), 204 (45), 146 (28), 102 (22), 91 (100). Anal. Calcd. for $C_{14}H_{13}NS_4$: C, 51.98; H, 4.05; N, 4.33. Found: C, 51.96; H, 4.16; N, 4.41. C.V.: $E_1^{1/2}$ = 0.29, $E_2^{1/2}$ = 0.67.

N-(4-methylphenyl)aminomethyltetrathiafulvalene **8c**: Yield (%): 30. M.p.(°C): 95-97.^{1}H-NMR δ: 2.23 (3H, s, CH_3), 3.86 (1H, br s, NH), 4.02 (2H, d, J = 1.1 Hz, CH_2), 6.15 (1H, t, J = 1.1 Hz, =CH), 6.28 (2H, s, =CH), 6.54 and 6.99 (4H, J_{app} = 8.4 Hz, Ar-H). ^{13}C-NMR δ: 20.4, 44.7, 109.9, 110.9, 113.2, 113.9, 119.0, 127.7, 129.8, 136.0, 144.7. EI MS m/z(%): 323 (M^+, 66), 217 (85), 204 (97), 146 (100), 120 (72), 102 (63), 91 (65). Anal. Calcd. for $C_{14}H_{13}NS_4$: C, 51.98; H, 4.05; N, 4.33. Found: C, 51.79; H, 4.17; N, 4.14. C.V.: $E_1^{1/2}$ = 0.32, $E_2^{1/2}$ = 0.70.

N-octadecylaminomethyltetrathiafulvalene **8d**: Yield (%): 15. M.p.(°C): 53-55.^{1}H-NMR δ: 0.86 (3H, t, J = 7 Hz, CH_3), 1.23 - 1.30 (32H, m, CH_2), 2.57 (2H, t, J = 7 Hz, N-CH_2), 3.54 (2H, d, J = 1.2 Hz, TTF-CH_2), 6.07 (1H, t, J = 1.2 Hz, =CH), 6.27 (2H, s, =CH). ^{13}C-NMR δ: 14.1, 22.6, 27.2, 29.3 - 29.9, 31.9, 48.9, 49.4, 110.1, 110.3, 113.3, 118.9, 119.1, 137.6. FAB MS m/z(%): 485 (M^+, 28), 217 (100). Anal. Calcd. for $C_{25}H_{43}NS_4$: C, 61.80; H, 8.92; N, 2.88. Found: C, 61.94; H, 8.97; N, 2.78. C.V.: $E_1^{1/2}$ = 0.29, $E_2^{1/2}$ = 0.67.

Aminomethyltetrathiafulvalene **9**: To a solution of formyltetrathiafulvalene **6** (0.232 g, 1 mmol) in a mixture of absolute ethanol (5 mL) / pyridine (5 mL), hydroxylamine hydrochloride (0.084 g, 1.2 mmol) is added at room temperature. The mixture is refluxed for 2 hours and the solvent is vacuum-distilled. Water (20 mL) is added to the residue and the mixture is stirred until an orange solid appears. The solid is filtered off, washed with water and dried. The crude oxime **10b** thus prepared is suspended in dry Et_2O (30 mL) under a nitrogen atmosphere and lithium aluminium hydride (0.019 g, 0.5 mmol) is added. The mixture is refluxed for 5 hours, after which excess hydride is destroyed as described in the case of compounds **8**. The organic solution is evaporated and the residue is purified on a silica column, first eluted with ether to discard less polar byproducts and then with ether - methanol 15:1 to afford pure compound **9** as a yellow oil.Yield based on **6** (%): 15. M.p.(°C): oil.^{1}H-NMR δ: 1.82 (2H, br s, NH_2), 3.60 (2H, d, J = 1.3 Hz, CH_2), 6.08 (1H, t, J = 1.3 Hz, =CH), 6.28 (2H, s, =CH). ^{13}C-NMR δ: 42.4, 110.0, 110.8, 112.7, 119.0, 119.1, 139.6. EI MS m/z(%): 233 (M^+, 91), 217 (6), 204 (60), 159 (33), 146 (100), 102 (77). Anal. Calcd. for $C_7H_7NS_4$: C, 36.03; H, 3.02; N, 6.00. Found: C, 36.19; H, 3.14; N, 5.94. C.V.: $E_1^{1/2}$ = 0.29, $E_2^{1/2}$ = 0.67.

Formyltetrathiafulvalene O-methyloxime **10a**: ^{1}H-NMR δ: 3.89 (3H, s, CH3), 6.29 (1H, d, J= 6 Hz, =CH), 6.31 (1H, d, J = 6 Hz, =CH), 6.55 (1H, s, =CH), 7.81 (1H, s, CH=N). EI MS m/z(%): 261 (M^+, 60), 230

(13), 203 (52), 146 (100), 102 (52).

Formyltetrathiafulvalene oxime **10b**: ^{1}H-NMR δ ($CDCl_3$ - DMSO-d_6): 6.27 (2H, s, =CH), 6.51 (1H, s, =CH), 7.86 (1H, s, CH=N). EI MS m/z: 247 (M^+), 203, 146, 102 (relative abundances not assigned, due to the presence of impurity peaks in the spectrum).

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REFERENCES AND NOTES

1. See, *inter alia*: (a) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355-390; (b) Williams, J. M.; Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwok, W.-K.; Whangbo, M.-H.; Schirber, J. E. *Science* **1991**, *252*, 1501-1508; (c) Proceedings of the ICSM'90, Tübingen, published in *Synth. Met.* **1991**, *41-43*; (d) *The Physics and Chemistry of Organic Superconductors*, ed. Saito, G. and Kagoshima, S., Springer-Verlag, London, **1990**.
2. (a) Poirier, D. M.; Ohno, T. R.; Kroll, G. H.; Chen, Y.; Benning, P. J.; Weaver, J. H.; Chibante, L. P. F.; Smalley, R. E. *Science* **1991**, *253*, 646-648; (b) Diederich, F.; Whetten, R. L. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 678-680.
3. (a) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Rep.* **1987**, *7*, 155-240; (b) Krief, A. *Tetrahedron* **1986**, *42*, 1209-1252. (c) Bryce, M. R. *Aldrichimica Acta* **1985**, *18*, 73-78; (d) Williams, J. M.; Wang, H.H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J. *Prog. Inorg. Chem.* **1987**, *35*, 51-218.
4. (a) Suzuki, T.; Yamochi, H.; Srdanov, G.; Hinkelmann, K.; Wudl, F. *J. Am. Chem. Soc.* **1989**, *111*, 3108-3109. (b) Wudl, F.; Yamochi, H.; Suzuki, T.; Isotalo, H.; Fite, C.; Kasmai, H.; Liou, K.; Srdanov, G. *J. Am. Chem. Soc.* **1990**, *112*, 2461-2462.
5. Larsen, J.; Lenoir, C. *Synthesis* **1989**, 134.
6. Papavassiliou, G.C.; Mousdis, G. A.; Zambounis, J. S.; Terzis, A.; Hountas, A.; Hilti, B.; Mayer, C. W.; Pfeiffer, J. *Synth. Met.* **1988**, *27*, B379-B383.
7. (a) Bryce, M. R.; Cooke, G. *Synthesis* **1991**, 263-265. (b) Becker, J. Y.; Bernstein, J.; Bittner, S.; Shahal, L.; Shaik, S. S. *J. Chem. Soc., Chem. Commun.* **1991**, 92-93. (c) Jorgensen, M.; Bechgaard, K. *Synthesis* **1989**, 207-208.
8. (a) Fourmigué, M.; Batail, P. *J. Chem. Soc., Chem. Commun.* **1991**, 1370-1372; (b) Fourmigué, M.; Batail, P. *Bull. Soc. Chim. France*, in press. (We thank the authors for providing us with a copy of their paper prior to its publication).
9. (a) Huang, Y. S.; Fourmigué, M.; Batail, P. unpublished work, cited in ref. 8(a); (b) Okamoto, Y.; Lee, H. S.; Attarwala, S. T. *J. Org. Chem.* **1985**, *50*, 2788-2790; (c) Bryce, M. R.; Cooke, G.; Dhindsa, A. S.; Lorcy, D.; Moore, A. J.; Petty, M. C.; Hursthouse, M. B.; Karaulov, A. I., *J. Chem. Soc., Chem. Commun.* **1990**, 816-818.
10. Terzis, A.; Hountas, A.; Underhill, A. E.; Clark, A.; Kaye, B.; Hilti, B.; Mayer, C.; Pfeiffer, J.; Yiannopoulos, S. Y.; Mousdis, G.; Papavassiliou, G.C. *Synth. Met.* **1988**, *27*, B97-B102.
11. Gorgues, A.; Batail, P.; Le Coq, A. *J. Chem. Soc., Chem. Commun.* **1983**, 405-406.
12. Chen, W.; Cava, M. P.; Takassi, M. A.; Metzger, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 7903-7904.
13. Bertho, F.; Robert, A.; Batail, P.; Robin, P. *Tetrahedron* **1990**, *46*, 433-444.
14. Fabre, J. M.; Garín, J.; Uriel, S. *Tetrahedron Lett.* **1991**, *32*, 6407-6410.

15. Jørgensen, M.; Lerstrup, K. A.; Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 5684-5688.
16. For the synthesis of tetrathiafulvalenes containing OH groups see, for instance: (a) Green, D.C. *J. Org. Chem.* **1979**, *44*, 1476-1479; (b) Bryce, M. R.; Marshallsay, G. J. *Tetrahedron Lett.* **1991**, *32*, 6033-6036; (c) Hsu, S.-Y.; Chiang, L. Y. *Synth. Met.* **1988**, *27*, B651-B656; (d) Hertler, W. R. *J. Org. Chem.* **1976**, *41*, 1412-1416; (e) Sallé, M.; Gorgues, A.; Fabre, J.-M.; Bechgaard, K.; Jubault, M.; Texier, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1520-1521.
17. Roberts, J. L.; Borromeo, P. S.; Poulter, C. D. *Tetrahedron Lett.* **1977**, *18*, 1299-1302.
18. Bryson, T. A.; Bonitz, G. H.; Reichel, C. J.; Dardis, R.E. *J. Org. Chem.* **1980**, *45*, 524-525.
19. Schaefer, M.; Weber, J.; Faller, P. *Bull. Soc. Chim. France* **1978**, 241-247.
20. Morimoto, T.; Takahashi, T.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1984**, 794-795.
21. Heaney, H.; Papageorgiou, G.; Wilkins, R. F. *J. Chem. Soc., Chem. Commun.* **1988**, 1161-1163.
22. Tramontini, M.; Angiolini, L. *Tetrahedron* **1990**, *46*, 1791 - 1837.
23. Pittman, C. U.; Narita, M; Liang, Y.F. *J. Org. Chem.* **1976**, *41*, 2855 - 2860.
24. Feuer, H.; Braunstein, D.M. *J. Org. Chem.* **1969**, *34*, 1817 - 1821.