



Pergamon

Tetrahedron Letters 41 (2000) 3083–3086

TETRAHEDRON
LETTERS

New planar and soluble tris-tetrathiafulvalene derivatives with threefold-symmetry

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Received 17 January 2000; accepted 25 February 2000

Abstract

Novel trimeric tetrathiafulvalene (TTF) derivatives with threefold-symmetry are built on the 1,3,5-benzene core. Long alkyl chains have been incorporated on the peripheral positions of the TTF moieties in order to increase the solubility of the final products. Electrochemical and spectroscopic studies of the target compounds suggest that there are no significant interactions between the TTF units because of their *meta* orientation. Semiempirical theoretical calculations indicate that the new systems exhibit a high structural anisotropy resembling that exhibited by discotic liquid crystals. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: tetrathiafulvalenes; electrochemistry; trimers.

Many efforts have been devoted in recent years to the development of new systems containing two or more tetrathiafulvalene (TTF) units^{1–3} as well as to the synthesis of star-shaped thiophene or TTF oligomers.⁴ Because of the intramolecular through-bond or through-space interactions between the TTF units, these kinds of systems may display multi-stage redox behaviour which might provide the possibility to control the stoichiometry, band filling and molecular assembly in desired conductive complexes. Depending upon the nature of the bridging groups between the TTF units and the geometry of the molecule, the intramolecular interaction between the redox moieties can be modified in a controlled way (Fig. 1).

Thus, although systems containing three TTF units should be oxidizable up to the hexacation, because each TTF unit can release two electrons, the number of electrochemical oxidation processes observed by using cyclic voltammetry measurements is strongly variable. Only two electrochemical processes corresponding to the oxidation to the trication and hexacation are observed for those systems in which the TTF units are not interacting⁵ while up to six electrochemical processes are observed for other systems with strong interactions between the TTF units.⁶

TTF dimers and trimers in which the TTF units are introduced at 1,3- or 1,3,5-positions of aromatic rings are especially interesting, given that a ferromagnetic interaction between TTF units might occur in the CT complex or radical-cation salts which are usually known to show conductivity. Thus, Iyoda and

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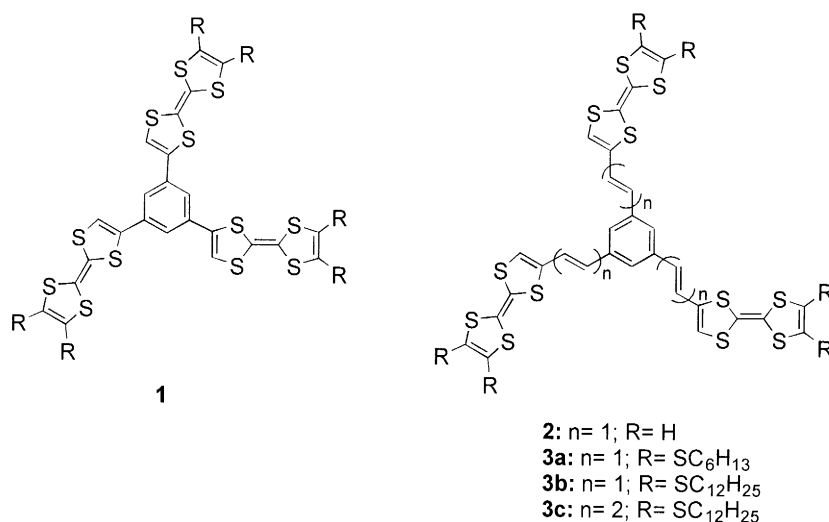


Fig. 1.

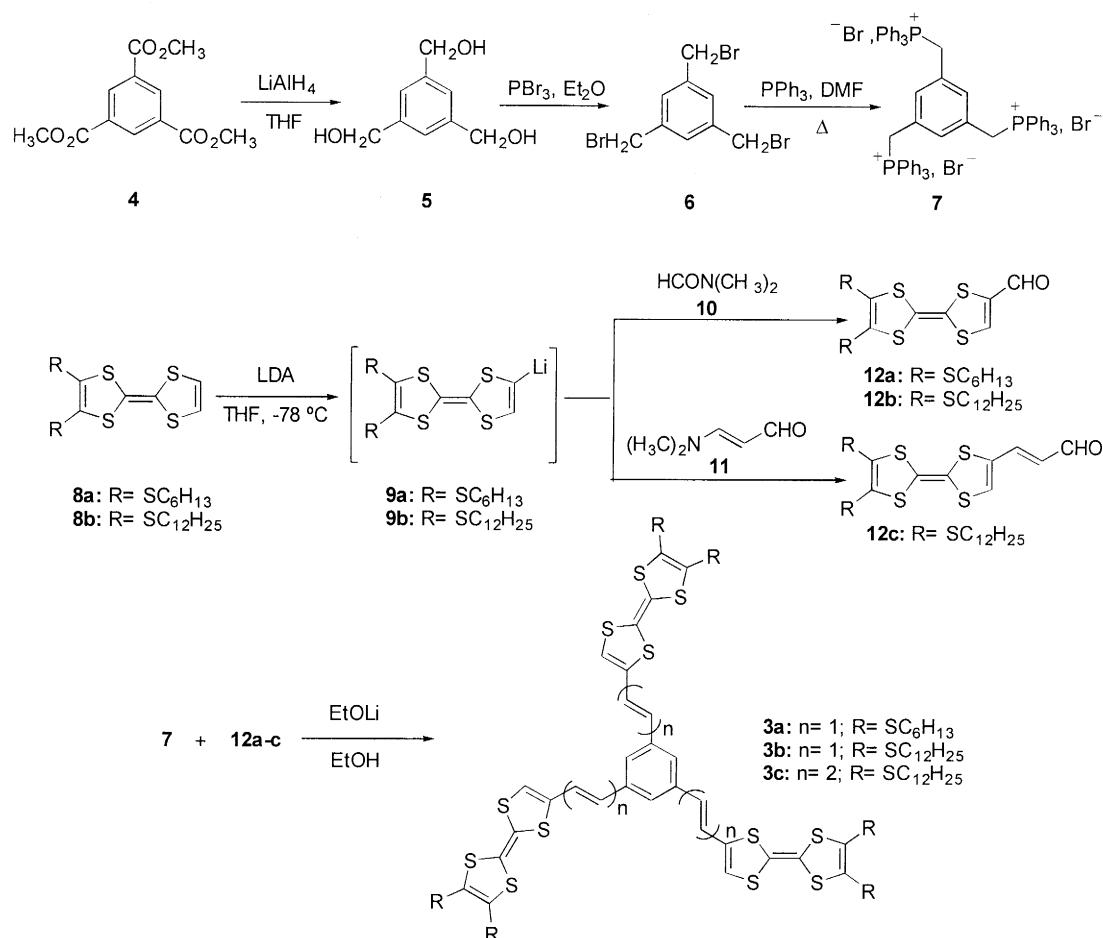
co-workers proposed that the triradical–trication salts derived from **1** should exhibit a quartet ground state if the three TTF radical cations show a ferromagnetic interaction.⁷ In 1993, Johannsen and co-workers attempted the synthesis of **2** which is the vinyllogue of trimer **1**.⁸ However, a dark red solid, insoluble in all usual solvents, was obtained but could not be investigated. In this communication we report the synthesis and the electrochemical and structural study of alkyl substituted analogues of **2** in which the presence of long alkyl chains efficiently improves their solubility in organic solvents, thus allowing appropriate spectroscopic and electrochemical characterization.

The synthesis of the hexakis(hexylthio)-, hexakis(dodecylthio)-derivatives **3a,b** as well as the hexakis(dodecyl)substituted vinyllogue **3c** were carried out following the synthetic route depicted in Scheme 1. The tris-(triphenylphosphonium) salt **7** was synthesized following the synthetic route previously reported by Storck and Manecke, starting from 1,3,5-tris-(methoxycarbonyl)benzene **4**.⁹ Reduction of **4** with lithium aluminium hydride followed by treatment with phosphorus tribromide yielded the 1,3,5-tris-(bromomethyl)derivative **6**. Reaction of **6** with triphenylphosphine in refluxing dimethylformamide afforded 1,3,5-tris-(triphenylphosphonium)benzene bromide **7** as a white solid that was used for the next synthetic step without further purification.

On the other hand, treatment of the dialkylthiosubstituted TTFs **8a,b** with LDA at -78°C in THF,¹⁰ followed by addition of either *N*-methylformanilide **10** or *N,N*-dimethylaminoacrolein **11**,¹¹ respectively, gave 4-formyl-4',5'-bis(alkylthio)tetrathiafulvalene **12a,b** and 4-(2-formylvinyl)-4',5'-bis(dodecylthio)tetrathiafulvalene **12c**.

Lithium ethoxide-catalyzed Wittig reaction of the tris-(triphenylphosphoniummethyl)benzene bromide **7** with formyl TTFs **12a–c** was carried out in chloroform:ethanol (3:5) at 50°C , leading to a mixture of various *cis/trans* isomers. Attempts at isomerization to the all-*trans* stereoisomer by using the usual iodine-catalyzed conditions was not successful due to the rapid formation of a charge-transfer salt between the TTF donor fragments and iodine. However, the major isomer (TLC) formed in the synthesis of compounds **3a–c** could be finally isolated by careful chromatography in moderate yields (30–50%).[†]

[†] Compounds **3a–c** gave satisfactory analytical and spectroscopic data. Selected spectroscopic data for **3a**: ¹H NMR (C₆D₆, 200 MHz): δ (ppm) 6.83 (s, 3H), 6.49 (d, 3H, $J=15.3$ Hz), 6.31 (d, 3H, $J=15.3$ Hz), 5.83 (s, 3H), 2.47 (t, 6H), 2.46 (t, 6H), 1.19 (m, 48H), 1.16 (m, 18H). ¹³C NMR (C₆D₆, 50 MHz): δ (ppm) 137.2, 135.9, 128.2, 119.3, 114.4, 109.3, 36.5, 31.6, 30.2, 28.5, 22.9, 14.2. Anal. calcd for C₆₆H₉₀S₁₈ (%): C: 54.32; H: 6.17; S: 39.51. Found: C: 54.20; H: 6.14; S: 39.72.



Scheme 1.

Spectroscopic analyses confirmed that the isolated isomers correspond to the more stable all-*trans* configurations, the coupling constant measured in the ¹H NMR spectra for the vinyl protons being around 16 Hz in all cases.

Cyclic voltammetry measurements (in dichloromethane, reference electrode: SCE; working electrode: platinum, supporting electrolyte: Bu₄N⁺ClO₄⁻, at 200 mV/s) performed for **3a–c** clearly confirm the lack of electronic interaction between the three TTF units in these systems. Thus, only two redox processes were observed, corresponding to the simultaneous oxidation of the three TTF units to the tris-(radical cation) (0.48 V) and hexacation (0.85 V) species.

Semiempirical theoretical calculations performed for systems **3** (AM1 level) show molecular geometries close to planarity. Fig. 2 depicts the minimum energy conformation obtained for **3a**. Long alkyl chains have been replaced by methyl groups in order to facilitate calculations. The minima obtained for these systems show a high structural anisotropy which resembles the disc form exhibited by discotic liquid crystals.

In conclusion, we have synthesized a new family of planar trimeric TTF systems with threefold symmetry, in which the TTF units are electronically independent. Because of the high structural anisotropy of these systems and the presence of the peripheral long alkyl chains, they are appealing candidates for the obtention of TTF-based discotic liquid crystals (LC). On the other hand, the *meta*

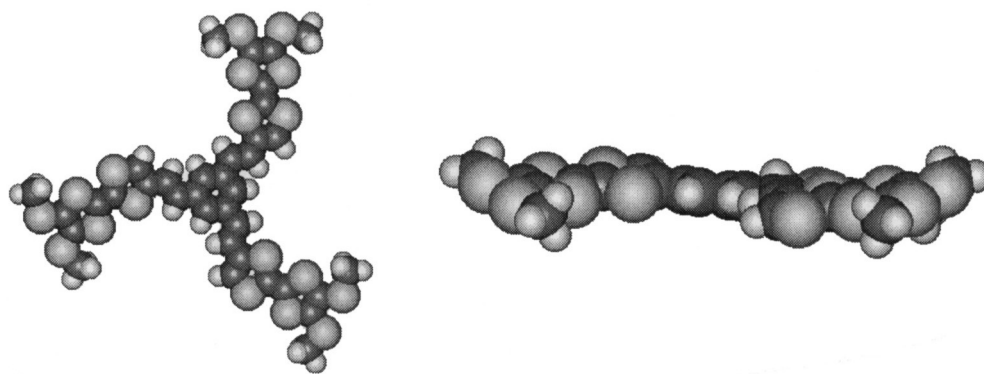


Fig. 2. Geometry of the most favourable conformation for **3a** determined by AM1 calculations

linking of the tetrathiafulvalene systems can produce interesting magnetic interactions in the charge-transfer salts of the trimers. Work is in progress in order to explore their potential behaviour as organic ferromagnets as well as LC in the search of novel multiproperty materials.

Acknowledgements

We are indebted to DGES of Spain (Project PB98-0818) for financial support.

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