ORGANIC LETTERS

2000
Vol. 2, No. 11
1585−1587

# New Chiral Binaphthyl Building Blocks: Synthesis of the First Optically Active Tetrathiafulvalene Dimers

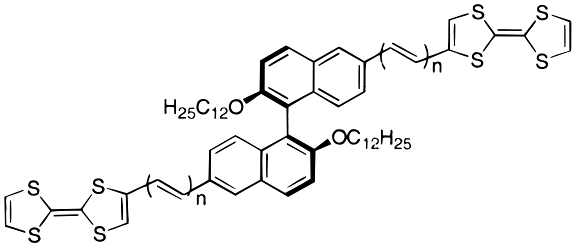
**Rafael Gómez, José L. Segura, and Nazario Martín***

*Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040-Madrid, Spain*

*nazmar@eucmax.sim.ucm.es*

Received March 16, 2000

## ABSTRACT



n= 1, 2

**New enantiomerically pure binaphthyl derivatives bearing triphenylphosphine or phosphonate groups have been synthesized and used as building blocks to prepare the first optically active tetrathiafulvalene dimers.**

The increase of dimensionality has been identified as a priority in chalcogenofulvalene chemistry in order to obtain improved electrically conducting materials. For this purpose, different strategies have been followed.[1] The introduction of heavy atoms at peripheral positions of the tetrathiafulvalene (TTF) moieties or the functionalization of the TTF system with OH or NRH groups that enable intermolecular hydrogen bonding can be considered as classical methods of achieving a different donor packing motif in CT complexes and/or salts. The concept of “crystal engineering” proposed by Desiraju[2] has also been applied in the field of molecular conductors to construct supramolecular assemblies.

Although much less explored, a promising strategy involves the design of nonplanar materials[3] and the use of spiroconjugation[4] as a way to add dimensionality in the design of organic molecular materials. For example, dimeric systems (**1**,[5] **2**,[6] Figure 1) where the two TTF units are connected through a spiro bond are able to form a two-dimensional column and $\pi$- and/or $\sigma$-interactions. In this Letter, we use funtionalized chiral binaphthyl units as a new approach for obtaining TTF dimers (**3**, Figure 1) in the search for enhanced dimensionality.

Binaphthyl derivatives are optically active materials, their chirality being derived from the restricted rotation of the two naphthalene rings. The angle between rings ranges from 60 to 120°, and therefore, these derivatives are ideal candidates to be used as nonplanar spacers between electroactive units. In addition, we have used vinyl spacers in **3a**,**b** in order to prevent the free rotation of the TTF units, resulting in two planar and rigid naphthalene−TTF moieties orthogonally arranged. Binaphthyl units have been used to construct a number of chiral rigid polymers[7] with main chain chirality which have found applications in areas such as asymmetric catalysis,[8] molecular recognition,[7] organic luminescence,[9] or

---

[1] Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481.

[2] (a) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (b) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.

[3] Kato, H.; Kobayashi, T. *Adv. Mater.* **1993**, *5*, 750.

[4] Maslak, P. *Adv. Mater.* **1994**, *6*, 405.

[5] Tatemitsu, H.; Nishikawa, E.; Sakata, H.; Misumi, S. *Synth. Met.* **1987**, *19*, 565.

[6] Ueda, K.; Yamanoha, M.; Sugimoto, T.; Fujita, H.; Ugawa, A.; Yakushi, K.; Kano, K. *Chem. Lett.* **1997**, 461.

[7] Pu, L. *Acta Polym.* **1997**, *48*, 116. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405.

10.1021/ol005821n CCC: $19.00

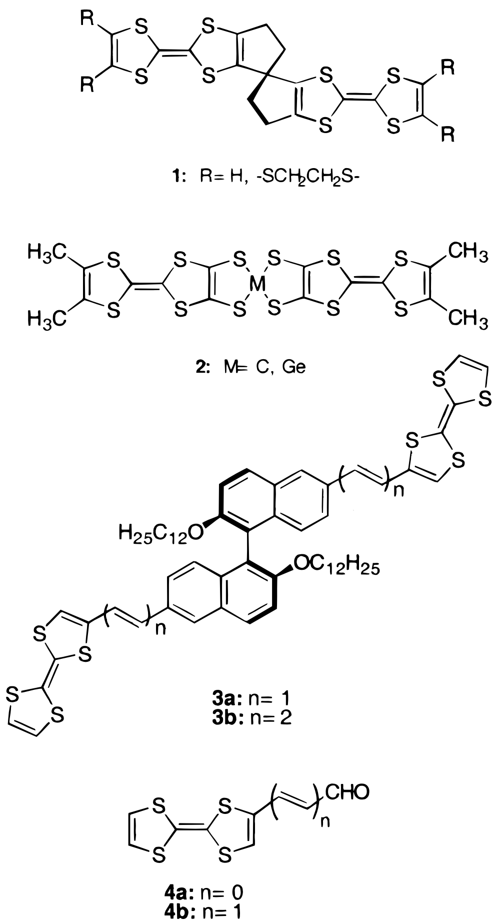
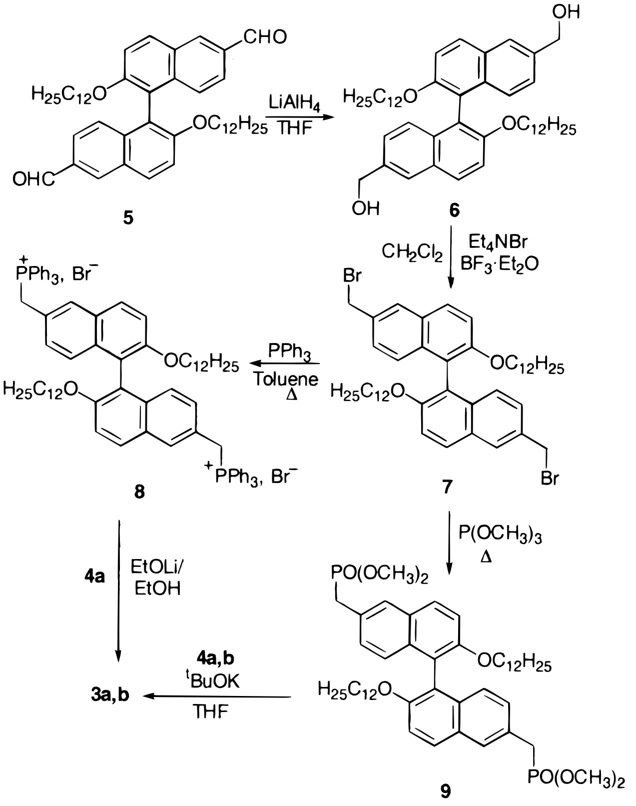


**Figure 1.** Dimeric systems **1** and **2** in which the two TTF groups are arranged by a spiro bond together with the new dimers **3a**,**b** and their precursors **4a**,**b**.

nonlinear optics.[10] However, to the best of our knowledge, the binaphthyl system has not been previously difunctionalized with triphenylphosphine or phosphonate groups. In this Letter we report the synthesis of enantiomerically pure, symmetrically functionalized binaphthyl derivatives bearing triphenylphosphonium (**8**) or methyl phosphonate (**9**) groups. These new and versatile building blocks can be further incorporated into a variety of molecular and polymeric materials through Wittig or Wittig−Horner olefination reactions.

The syntheses of **8** and **9** have been carried out from enantiomerically pure (*R*)-2,2′-didodecyloxy-6,6′-diformyl-1,1′-binaphthyl (**5**).[9] Reduction of **5** with lithium aluminum hydride in dry THF yielded the (*R*)-bis(hydroxymethyl) derivative **6**, which upon treatment with tetraethylammonium bromide and boron trifluoride etherate in dry dichloromethane afforded the (*R*)-bis(bromomethyl) derivative **7**. (*R*)-Bisphosphonium dibromide (**8**) was obtained from **7** by treatment with triphenylphosphine in refluxing toluene for 4 h. (*R*)-Bisphosphonate (**9**) could be similarly obtained from **7** upon heating in trimethyl phosphite followed by chromatographic purification (Scheme 1).

**Scheme 1**



The target compounds **3a**,**b** were obtained by using both Wittig and Wittig−Horner reactions. When a mixture of bis(triphenylphosphonium)salt **8** and formyl TTF **4a** in dry ethanol was heated at 50 °C for 90 min using lithium ethoxide as a base, dimer **3a** was isolated in a 69% yield as a mixture of *cis*/*trans* isomers. $^1$H NMR spectroscopy showed that the major compound was the *all-trans* derivative ($J_{trans}$ = 15.9 Hz) and less than 10% of the *all-cis* derivative ($J_{cis}$ = 12.0 Hz) could be observed. However, we were not able to separate both isomers chromatographically. Attempts at *cis*/*trans* isomerization by heating a toluene solution of **3a** in the presence of iodine produced a dark mixture due, probably, to the formation of the radical-ion salt of the TTF derivative.

As an alternative to the above Wittig reaction, we performed Wittig−Horner reactions between phosphonate **9** and formylTTF **4a** and its vinylogue **4b**.[11] To a solution of **9** and the corresponding formylTTF **4** in dry THF was added potassium *tert*-butoxide, and the mixture was stirred at room temperature for 1.5 h. After extraction of the reaction crude

---

(8) Yu, H.-B.; Zheng, X.-F.; Lin, Z.-M.; Hu, Q.-S.; Huang, W.-S.; Pu, L. *J. Org. Chem.* **1999**, *64*, 8149 and references therein.

(9) Gómez, R.; Segura, J. L.; Martín, N. *Chem. Commun.* **1999**, 619.

(10) Deussen, H.-J.; Boutton, C.; Thorup, T.; Geisler, T.; Hendrickx, E.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *Chem. Eur. J.* **1998**, *4*, 240.

(11) Gónzalez, M.; Martín, N.; Segura, J. L.; Garín, J.; Orduna, J. *Tetrahedron Lett.* **1998**, *39*, 3269.

with methylene dichloride, the solvent was removed under vacuum and the residue was chromatographed to yield TTF dimer **3a** and its vinylogue **3b** as stable red solids. Although lower yields were obtained (around 15%) for the TTF dimers, Wittig−Horner reactions afforded solely the *all-trans* configuration product. The presence of the long alkyl chains on the binaphthyl moiety resulted in highly soluble TTF dimers which allowed spectroscopic and electrochemical characterization.[12] As the dimers were synthesized by using enantiomerically pure (*R*)-binaphthyl derivatives (**8**, **9**), chiral compounds were obtained. The observed optical rotations ($[\alpha_D]$) are −221.2° ($c = 3.3 \times 10^{-4}$, $CHCl_3$) for **3a** and −587.9° ($c = 3.3 \times 10^{-4}$, $CHCl_3$) for **3b**.

The electronic spectra (in dichloromethane) of the dimers exhibit, together with the characteristic bands corresponding to the TTF and the binaphthyl systems, a band at 432 nm for **3a** and at 436 nm for **3b** which can be assigned to the conjugated system formed by the TTF moiety, the vinyl groups, and the naphthalene ring of the binaphthyl system.

The cyclic voltammogram of these new donors ($CH_2Cl_2$, SCE as reference electrode, glassy carbon as working electrode, $\upsilon = 200$ mV/s) shows two two-electron reversible redox waves at $E^1_{ox} = 0.52$ V and $E^2_{ox} = 0.90$ V for **3a** and $E^1_{1/2} = 0.48$ V and $E^2_{1/2} = 0.84$ V for **3b** (for comparison, TTF: $E^1_{1/2} = 0.37$ V; $E^2_{1/2} = 0.67$ V). The two TTF units are thus oxidized independently to form bis(radical-cation) and tetracation species.

Because of the good donor ability of these TTF dimers, we have carried out the formation of charge-transfer complexes. Thus, when two refluxing dichloromethane solutions of dimers **3** and dichlorodicyano-*p*-benzoquinone (DDQ) were mixed, the respective charge-transfer complex precipitated as a black solid. Work is in progress to determine the crystal structure of the charge-transfer complexes which will confirm whether two-dimensional stacking provided by the binaphthyl spacer takes place.

In summary, new optically active TTF dimers containing binaphthyl units have been synthesized. They show good donor ability and form charge-transfer complexes in combination with DDQ. The bidimensional nature of the binaphthyl unit produces materials with enhanced dimensionality. Finally, this approach may provide an effective method for synthesizing different chiral molecular and polymeric materials containing binaphthyl units by using the effective Wittig and Wittig−Horner reactions.

**Acknowledgment.** This work has been supported by the DGESIC of Spain (Project PB98-0818). R.G. is indebted to the European Commission (Contract JOR3CT980206). We are also indebted to Centro de Espectroscopía de la UCM.

OL005821N

---

(12) Dimers **3** were characterized on the basis of the FT-IR, $^1$H and $^{13}$C NMR, and elemental analyses for which satisfactory results were obtained. Selected spectroscopical data for **3a**: FT-IR $\nu$ (KBr) = 3018, 2926, 2852, 1624, 1466, 1261, 1215, 750 cm$^{-1}$; $\delta_H$ ($CDCl_3$, 300 MHz) 7.82 (d, 2 H, $J$ = 9.0 Hz), 7.78 (s, 2 H), 7.38 (d, 2 H, $J$ = 8.8 Hz), 7.31 (d, 2 H, $J$ = 8, 8 Hz), 7.09 (d, 2H, $J$ = 8.8 Hz), 6.88 (d, 2H, $J$ = 15.9 Hz), 6.53 (d, 2 H, $J$ = 15.9 Hz), 6.33 (s, 6H), 3.95−3.88 (m, 4H), 1.49 (s, 4H), 1.34−0.84 (m, 40H), 0.79 (t, 6H); $\delta_C$ ($CDCl_3$, 75 MHz) 136.2, 133.9, 132.3, 131.4, 129.4, 129.1, 127.2, 125.9, 123.3, 120.4, 119.5, 118.9, 117.6, 115.9, 112.2, 108.7, 69.5, 32.0, 29.7, 29.5, 29.4, 29.3, 29.1, 25.7, 22.7, 14.1. Anal. Calcd for $C_{60}H_{70}O_2S_8$: C, 66.74; H, 6.53. Found: C, 65.85; H, 6.71.