

## Bridged 1,6-Dithienylhexa-1,3,5-trienes as Highly Photoluminescent and Stable Thiophene-Based $\pi$ -Conjugated Systems

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Bi- and tricyclic bridged dithienyl-1,3,5-hexatrienes (**2** and **3**) have been synthesized by McMurry dimerization of fused multicyclic ketones. The experimental conditions for the preparation of the precursor ketones have been established through a detailed analysis of the Robinson annulation of cyclopenta[*b*]thiophen-6-ones. The structures and electrochemical and optical properties of compounds **2** and **3** have been investigated using the open-chain analogue **1** as a reference. Whereas X-ray data confirm the highly conjugated and rigid structure of the bridged compounds, cyclic voltammetry and UV–vis and photoluminescence spectroscopy show that rigidification of the  $\pi$ -conjugated system produces a significant decrease in oxidation potential and HOMO–LUMO gap and a considerable enhancement of the photoluminescence quantum yield and thermal stability.

### Introduction

The electronic properties of linear  $\pi$ -conjugated systems (LCSs) have been the focus of considerable current theoretical and experimental interest.<sup>1–5</sup> In addition to their potential use as molecular wires in future molecular electronic devices,<sup>2</sup> LCSs have also acquired a growing importance as electron relays in chromophores for non-linear optics (NLO)<sup>3</sup> or as active components in electronic devices<sup>4</sup> or light-emitting diodes (LEDs).<sup>5</sup>

Since most of the relevant electronic properties of LCSs such as electron transmission efficiency, concentration of intrinsic charge carriers, ionization potential and electron affinity, and absorption and emission spectra are

directly related to the HOMO and LUMO levels and to the width of the HOMO–LUMO gap, the molecular engineering of these parameters has become a major concern for synthetic chemists. While optimal  $\pi$ -electron delocalization remains crucial for the design of molecular wires or push–pull NLO-phores,<sup>1–3</sup> progress in the field of organic LEDs requires the synthesis of  $\pi$ -conjugated fluorophores with tailored luminescence spectra and high emission quantum yields. Furthermore, molecules designed for both purposes should present optimized thermal stability.<sup>4,6</sup>

Whereas the HOMO–LUMO gap ( $\Delta E$ ) of polyenic systems depends essentially on bond length alternation,<sup>7</sup> for (hetero)aromatic-based systems the aromatic resonance energy of the cycle and the rotational disorder also play a determining role.<sup>1</sup> Since the first synthesis of poly-(isothianaphthene),<sup>8a</sup> the increase of the quinonoid character of the conjugated backbone to the detriment of its aromaticity has represented the main strategy for synthesizing small band gap aromatic LCSs.<sup>1,8</sup> While this research area remains active,<sup>8</sup> during the past few years the rigidification of the  $\pi$ -conjugated system has emerged as an interesting alternative strategy.<sup>9,10</sup> While the efficiency of this approach has been demonstrated for various series of benzenic<sup>9</sup> or thiophenic<sup>10</sup> LCSs, the smaller gap of thiophene-based systems has underlined

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(1) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(2) (a) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687. (b) Effenberger, F.; Schlosser, H.; Bäuerle, P.; Maier, S.; Port, H.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 281. (c) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348. (d) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906. (e) Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, *119*, 10774. (f) Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 942.

(3) (a) Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, *5*, 804. (b) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21. (c) Nalwa, H. S. *Adv. Mater.* **1993**, *5*, 341. (d) Marder, S. R.; Torruellas, W. E.; Blanchard-Desce, M.; Ricci, V.; Stegeman, G. I.; Gilmour, S.; Brédas, J. L.; Li, J.; Bublitz, G. U.; Boxer, S. G. *Science* **1997**, *276*, 1233.

(4) (a) Tasaka, S.; Katz, H. E.; Hutton, R. S.; Orenstein, J.; Frederickson, G. H.; Wang, T. T. *Synth. Met.* **1986**, *16*, 17. (b) Fichou, D.; Nishikitani, Y.; Horowitz, G.; Roncali, J.; Garnier, F. *Synth. Met.* **1989**, *28*, C729. (c) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716. (d) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684. (e) Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270. (f) Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369.

(5) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47. (c) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477. (d) Berggren, M.; Inganäs, O.; Gustafsson, G.; Rasmussen, J.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *Nature* **1994**, *372*, 444.

(6) Gymer, R. W. *Endeavour* **1996**, *20*, 115.

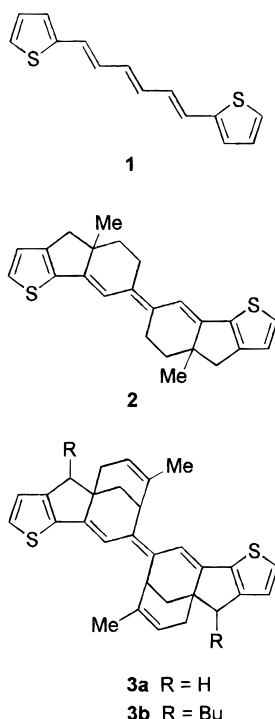
(7) Brédas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808. Kertesz, M.; Lee, Y.-S. *J. Phys. Chem.* **1987**, *91*, 2690.

(8) (a) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382. (b) Jenekhe, S. *Nature* **1986**, *322*, 345. (c) Lorcy, D.; Cava, M. P. *Adv. Mater.* **1992**, *4*, 562. Bäuerle, P.; Götz, G.; Emerle, P.; Port, H. *Adv. Mater.* **1992**, *4*, 564.

(9) (a) Scherf, U.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489. (b) Schlüter, A. D.; Löfner, M.; Enkelmann, V. *Nature* **1994**, *368*, 331.

(10) (a) Brisset, H.; Thobie-Gautier, C.; Gorgues, A.; Jubault, M.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1305. (b) Brisset, H.; Thobie-Gautier, C.; Jubault, M.; Gorgues, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1765. (c) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846. (d) Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E.; Frère, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2249. (e) Brisset, H.; Blanchard, P.; Illien, B.; Riou, A.; Roncali, J. *Chem. Commun.* **1997**, 569. (f) Blanchard, P.; Brisset, H.; Illien, B.; Riou, A.; Roncali, J. *J. Org. Chem.* **1997**, *62*, 2401.

Chart 1



the role of the aromatic stabilization energy<sup>11</sup> of the cycle in the gap width. This suggests that a possible way to achieve a further decrease of the overall aromaticity of the LCS could consist of the insertion of a polyenic spacer between the thiophene rings. However, such an approach is severely limited by the poor thermal stability of polyenes.

In an attempt to sort out this dilemma, we have undertaken the synthesis of 1,6-dithienylhexa-1,3,5-trienes rigidified by multiple bridging of the polyenic system (**2** and **3**) (Chart 1). These compounds have been synthesized by a McMurry coupling reaction of polycyclic precursor ketones (**9** and **10**) obtained through a detailed analysis of the Robinson annulation reaction of cyclopenta[*b*]thiophen-6-ones (**4**).

We report here the synthesis of the target compounds (**2** and **3**) and the characterization of their structures and electrochemical and optical properties. On the basis of X-ray data, cyclic voltammetry, UV-vis and fluorescence spectroscopy and differential scanning calorimetry, the effects of rigidification on the electronic properties and thermal stability of the  $\pi$ -conjugated system are discussed using the open-chain analogue **1** as a reference compound.

## Results and Discussion

**Synthesis.** The open-chain compound **1** was prepared using a known procedure.<sup>12</sup> The synthesis of the fused-ring conjugated ketones **9a,b** and **10** by Robinson annulation of cyclopenta[*b*]thiophen-6-ones (**4**) represents the key step in the preparation of the target compounds. Robinson annulation basically involves the Michael addition of a ketone to methyl vinyl ketone (MVK), followed

by aldol condensation.<sup>13</sup> This reaction leads to the construction of a cyclohexenone ring onto a preexisting ketone. On such a basis, one may in principle envisage repeating the procedure in order to achieve the stepwise extension of the bridged conjugated system. However, as shown below, achievement of double annulation requires drastic structural conditions in order to prevent the formation of numerous byproducts.

The starting materials, i.e. the unsubstituted cyclopenta[*b*]thiophen-6-one (**4a**),<sup>14</sup> the 5-methyl derivative (**4c**)<sup>15</sup> and the butyl-substituted ketone (**4b**),<sup>10f</sup> were synthesized using known procedures. In a first set of experiments, reaction of **4a** with 1 equiv of MVK under basic conditions led to the recovery of 45% of unreacted starting material, while the target compound **5** was isolated in low yield (3%) and two different byproducts were identified (Scheme 1). The first results from dialkylation of **4a** at the  $\alpha$ -position of the carbonyl followed by aldol-type ring closure to give the spiro keto alcohol **6** as a mixture of the two diastereomers **6'** and **6''**, the second being the keto alcohol **7a**. Although **6** was first detected by mass spectrometry, definitive structure confirmation was obtained after a further dehydration reaction of **6'** leading to **8**, which was identified by the usual analyses and <sup>1</sup>H NMR studies (COSY and decoupling experiments). Note that when the inseparable mixture of **6''** and **7a** was subjected to the previous treatment, only **6''** was dehydrated to give **8**, thus allowing separation of unreacted **7a**. Compound **7a** can in turn be dehydrated using H<sub>2</sub>SO<sub>4</sub> in refluxing toluene. The different reactivities of **6** and **7a** can be related to the easy formation of an  $\alpha,\beta$ -unsaturated ketone (**8**) from **6**, whereas this is geometrically hindered from **7a**.

Formation of **7a** can be rationalized on the basis of Scheme 2. A first deprotonation at the  $\gamma$ -carbon of ketone **5** leads to further alkylation with MVK, followed by deprotonation at the  $\alpha$ -position of the conjugated ketone and subsequent attack of the acetyl group by the resulting anion. Thus, **7a** results from a bis-annulation of **4a** via compound **5**, which explains the poor yield of this latter compound. This has two consequences. First, examination of the structure of compound **9a**, namely the dehydration product of **7a** (see Scheme 3), shows that this doubly bridged ketone can be also an interesting starting material for further synthesis of bridged dithienyl polyenes. Second, the preparation of ketone **5** in reasonable yield implies prevention of the deprotonation at the  $\gamma$ -carbon. On the basis of these conclusions, subsequent work was focused on the deliberate preparation of type **9** and **5** ketones.

Thus, addition of 2 equiv of MVK to **4a** in the presence of KOH led to a diastereomeric mixture of **7a**, which was directly dehydrated to give ketone **9a** in 28% overall yield based on **4a** (Scheme 3). It should be underlined that this yield is rather exceptional in view of the poor yield generally associated with Robinson annulation<sup>13</sup> and of the numerous intermediate compounds involved in the synthesis of **9a**.

(11) Hernandez, V.; Castiglioni, C.; Del Zopo, M.; Zerbi, G. *Phys. Rev. B* **1994**, *50*, 9815.

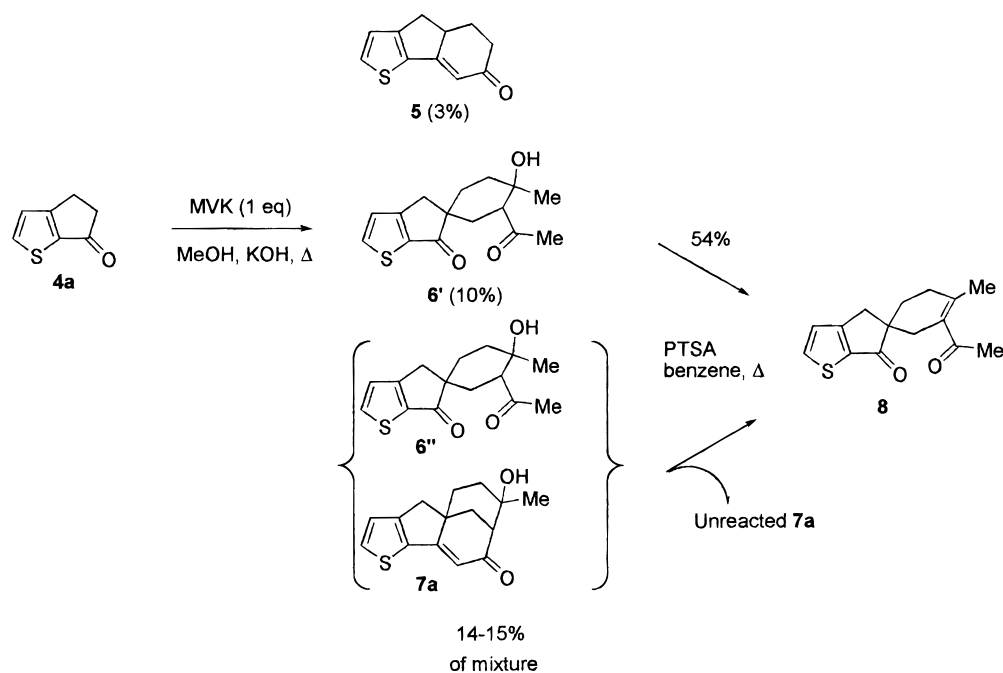
(12) (a) Miller, R. E.; Nord, F. F. *J. Org. Chem.* **1951**, *16*, 1380. (b) Spangler, C. W.; Liu, P. K.; Dembek, A. A.; Avelka, O. *J. Chem. Soc., Perkin Trans. 1* **1991**, 799.

(13) (a) Rapson, W. S.; Robinson, R. *J. Chem. Soc.* **1935**, 1285. (b) Jung, M. E. *Tetrahedron* **1976**, *32*, 3. (c) Gawley, R. E. *Synthesis* **1976**, 777. (d) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179.

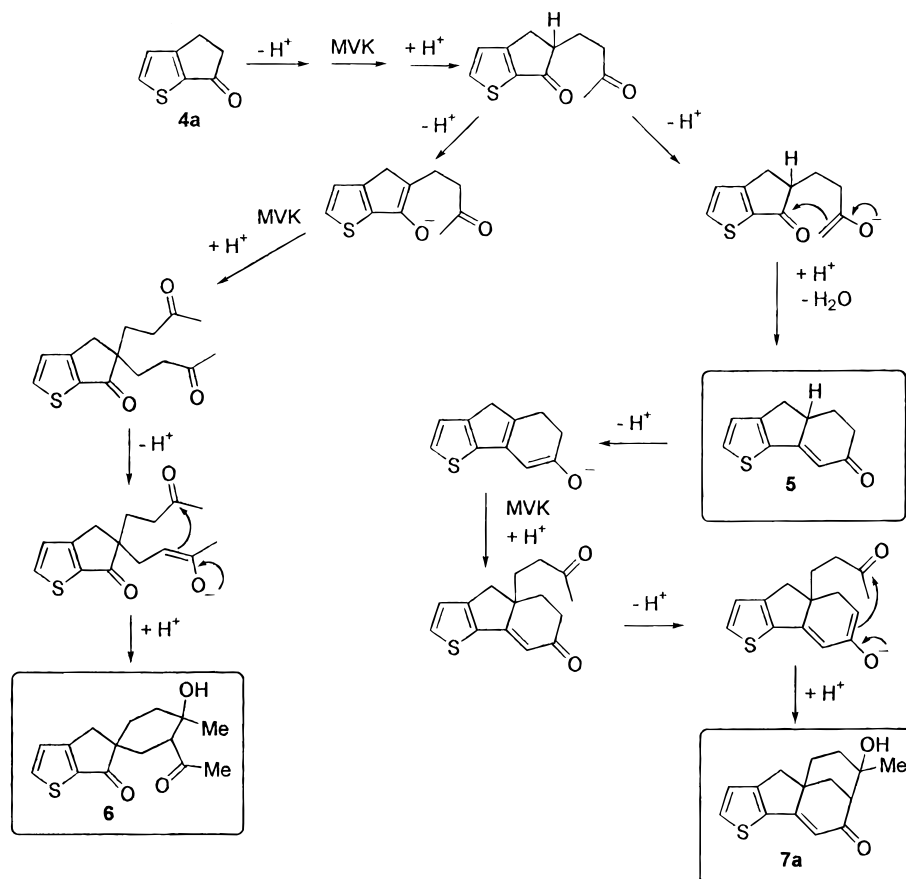
(14) MacDowell, D. W. H.; Patrick, T. B.; Frame, B. K.; Ellison, D. L. *J. Org. Chem.* **1967**, *32*, 1227.

(15) (a) Blicke, F. F.; Burckhalter, J. H. *J. Am. Chem. Soc.* **1942**, *64*, 451. (b) Burckhalter, J. H.; Sam, J. *J. Am. Chem. Soc.* **1951**, *73*, 4460.

## Scheme 1



## Scheme 2



A single crystal of **9a** has been analyzed by X-ray diffraction, and the corresponding data are listed in Table 1. The X-ray structure (not shown) reveals a nearly planar conjugated system with the 1-methyl prop[1]eno bridge lying in a plane roughly perpendicular to that of the conjugated system.

Application of the above procedure to ketone **4b** afforded the corresponding bis-annulated ketone **9b** in 15%

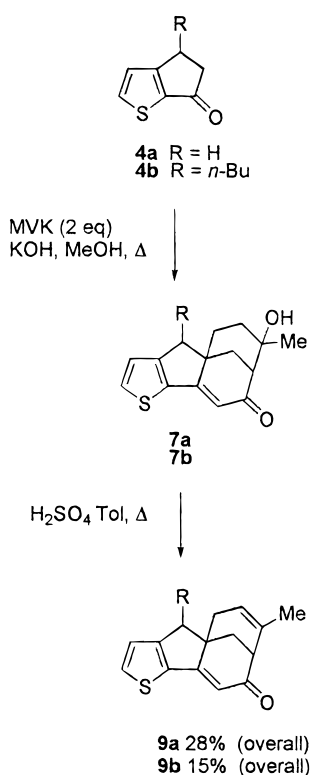
overall yield (Scheme 3). As a consequence of substitution, **9b** is obtained as a mixture of diastereomers (see Experimental Section).

To deliberately orient annulation toward the target type **5** ketone (**10**), reaction was carried out using ketone **4c**<sup>10f,15</sup> in which a second deprotonation is prevented by the methyl group at the  $\alpha$ -position of the carbonyl group. Reaction under basic conditions with a slight excess of

Table 1. Crystallographic Data for Compounds **5**, **9a**, and **Z-3a**

compd	<b>5</b>	<b>9a</b>	<b>Z-3a</b>
mol formula	C <sub>11</sub> H <sub>10</sub> OS	C <sub>15</sub> H <sub>14</sub> OS	C <sub>30</sub> H <sub>28</sub> S <sub>2</sub>
fw	190.05	242.34	452.67
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>C2/c</i>	<i>P1</i>	<i>P2<sub>1</sub>/c</i>
<i>T</i> (K)	298	298	298
<i>a</i> (Å)	17.297(13)	7.120(3)	14.444(20)
<i>b</i> (Å)	10.328(14)	8.953(2)	10.943(6)
<i>c</i> (Å)	11.853(14)	10.177(4)	15.198(17)
$\alpha$ (deg)		93.29(3)	
$\beta$ (deg)	116.2	106.76(3)	100.05(10)
$\gamma$ (deg)		100.22(3)	
<i>V</i> (Å <sup>3</sup> )	1900	607.2(4)	2365.33(45)
<i>Z</i>	8	2	4
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.33	1.325	1.268
$\mu$ (cm <sup>-1</sup> )	2.81	1.171	2.304
diffractometer	MACH3	MACH3	MACH3
scan	$\omega$ scan	$\omega$ scan	$\omega$ scan
radiation (Mo K $\alpha$ )	$\lambda = 0.71073$ Å	$\lambda = 0.71073$ Å	$\lambda = 0.71073$ Å
monochromator	graphite	graphite	graphite
no. of std rflns	3	3	3
decay of stds, %	2	2	2
no. of rflns measd	15	3791	6940
$2\theta$ range (deg)	$3 < \theta < 28$	$2 < \theta < 30$	$2 < \theta < 30$
range of <i>h, k, l</i>	<i>h</i> (0–17), <i>k</i> (0–13), <i>l</i> (–14 to +14)	<i>h</i> (0–10), <i>k</i> (–12 to +12), <i>l</i> (–14 to +14)	<i>h</i> (0–20), <i>k</i> (0–15), <i>l</i> (–21 to +21)
no. of rflns obsd with $I > 3\sigma(I)$	1351	2847	2360
corrections applied	Lorentz polarization and absorption	Lorentz polarization and absorption	Lorentz polarization and absorption
computer program	Molen	Molen	Molen
no. of variables	118	154	289
<i>R</i>	0.16	0.076	0.070
<i>R<sub>w</sub></i>	0.20	0.098	0.086

## Scheme 3



MVK leads to the consumption of all starting material with formation of three products (Scheme 4). The target ketone **10** was obtained in modest yield (12%), the major product (**11**) (53%) resulting from monoalkylation at the  $\alpha$ -position of the carbonyl group. A  $\beta$ -deprotonation and subsequent aldolization of this latter compound can account for the formation of the keto alcohol **12** (10%).

The structure of this compound was deduced from that of its dehydrated derivative **13**. Aldol condensation of diketone **11** and further in situ dehydration afforded the target ketone **10** in 54% yield together with 20% of keto alcohol **12**.

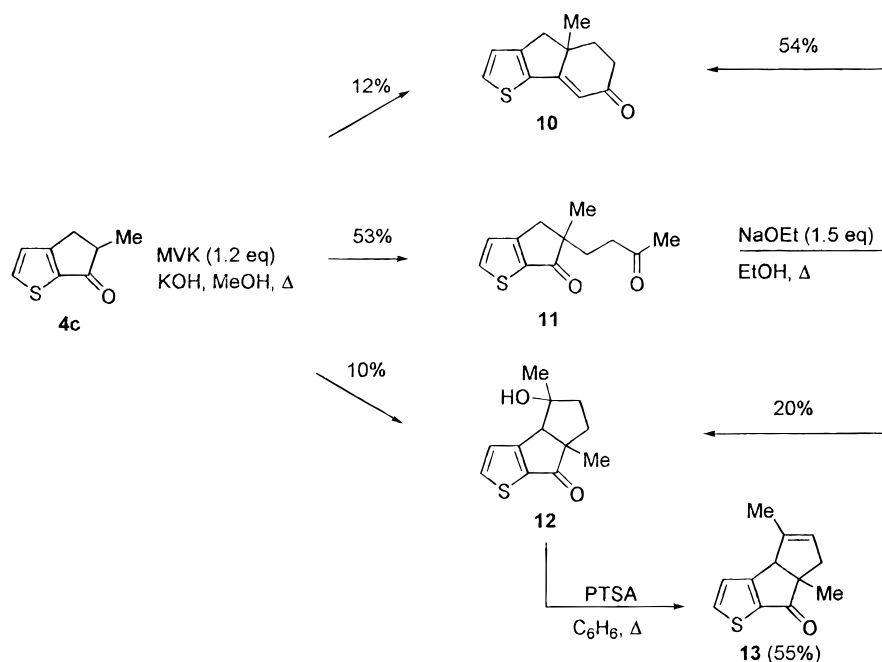
Ketones **10** and **9a,b** were then subjected to a McMurry reaction,<sup>16</sup> which led in good yields to the extended bicyclic (**2**) and tricyclic (**3a,b**) systems (Scheme 5). All these compounds were obtained as mixtures of diastereomers due to the presence of chiral carbons and to possible *E/Z* isomerization around the central double bond. Thus, for **3a** four diastereomers were expected. Column chromatography gave two fractions: the first (F1) contained two diastereomers (100:12, as shown by <sup>1</sup>H NMR), while the second (F2) contained essentially one. Recrystallization of F2 gave crystals of a pure diastereomer which were analyzed by X-ray diffraction.

Figure 1 shows the ORTEP view of a single crystal obtained from the second fraction (**Z-3a**). The median double bond (C11a–C11b) adopts a *Z* configuration associated with a slightly curved  $\pi$ -conjugated backbone. The two exocyclic bridges lie on two opposite sides of the molecule so that the  $\pi$ -conjugated system is doubly locked within two perpendicular planes. The fact that no diastereomer with the two bridges on the same side of the molecule has been detected can be related to the steric hindrance that would result from interactions between the methyl groups. On the basis of these observations it can be inferred that the two diastereomers observed in F1 correspond to an *E* configuration of the central double bond (**E-3a**), in agreement with UV–vis data (see below).

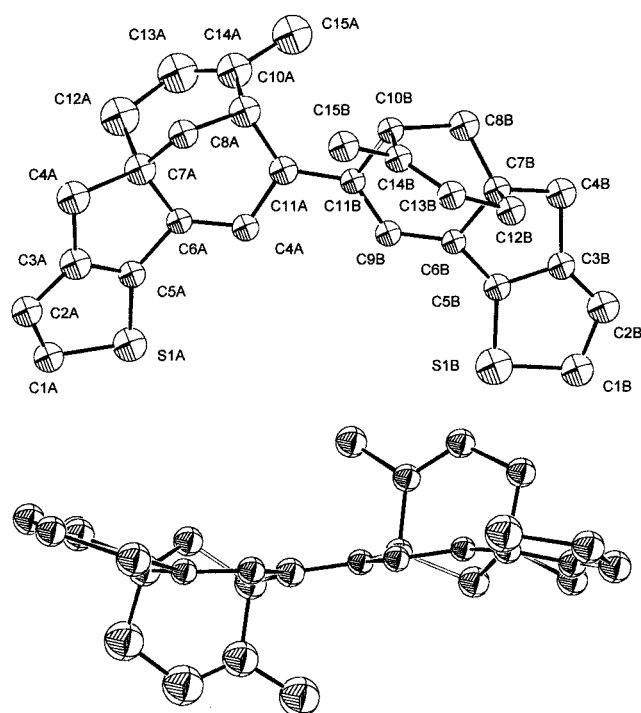
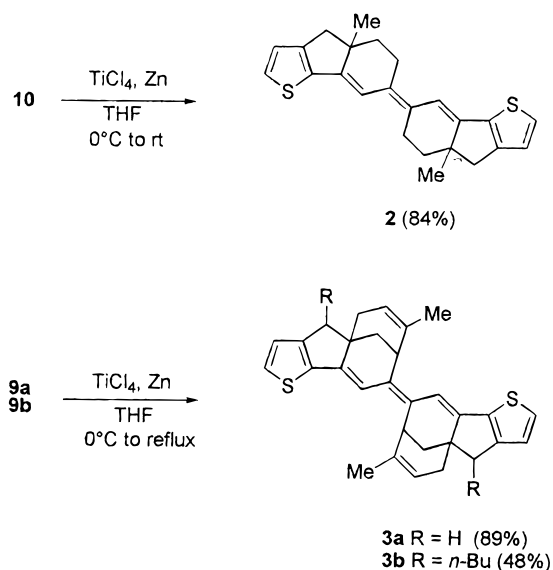
TLC of **3b**, which contains two additional asymmetric

(16) (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513. (b) Förstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2443.

## Scheme 4



## Scheme 5

Figure 1. ORTEP view of compound **Z-3a**.

carbons, shows four close spots. The fractions collected by column chromatography were gathered to give a yellow oil containing a mixture of diastereomers. Although compound **2** shows only one spot in TLC,  $^1H$  NMR suggests the presence of different diastereomers.

In addition to a confirmation of their molecular structure, the electron-impact mass spectra of **2** and **3** exhibit essentially an intense peak corresponding to the molecular ion. The occurrence of very few fragmentations reveals a high stability of the molecular ions, whereas the relatively intense peaks at half the molecular weight suggest an easy access to the dication.

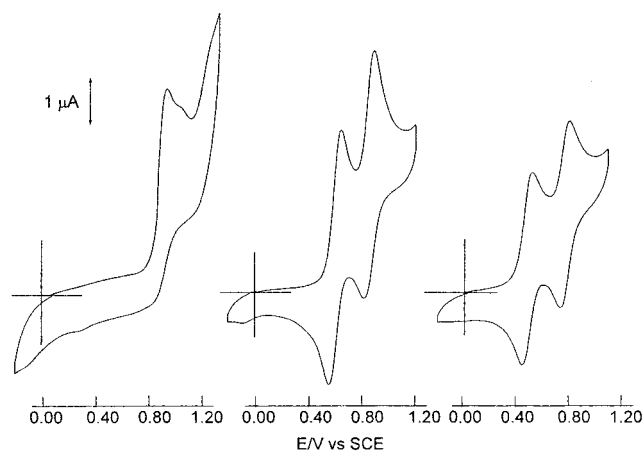
**Cyclic Voltammetry.** The cyclic voltammogram (CV) of **1** shows two irreversible anodic waves peaking at 0.95 V ( $E_{p,a}^1$ ) and 1.25 V ( $E_{p,a}^2$ ) corresponding to the successive generation of the cation radical and dication (Figure 2). The peak of low intensity at 1.05 V is related to some aggregation phenomena as confirmed by its disappearance upon dilution.<sup>17</sup> The irreversibility of the first

anodic wave indicates a follow-up chemical reaction corresponding to the electropolymerization of **1**.<sup>18</sup>

As shown in Figure 2, with rigidification of the conjugated system the two oxidation processes become fully reversible, while  $E_{p,a}^1$  shifts negatively by ca. 0.30 V for compounds **3** and by 0.44 V for **2** (Table 2). These lower oxidation potentials suggest an extension of effective conjugation, as confirmed by optical data. Table 2

(17) Roncali, J.; Jubault, M.; Gorgues, A. *Chem. Mater.* **1993**, *5*, 1456.

(18) (a) Tanaka, S.; Sato, M.; Kaeriyama, K. *Makromol. Chem.* **1985**, *186*, 1685. (b) Bäuerle, P.; Wrighton, M. S.; Chyan, O. M. R.; Spangler, C. R. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 889.



**Figure 2.** Cyclic voltammograms of dithienylhexatrienes (ca.  $10^{-3}$  M in  $10^{-1}$  M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ ; scan rate  $100 \text{ mV s}^{-1}$ ): (left) **1**; (middle) **Z-3a**; (right) **2**.

**Table 2. Cyclic Voltammetric Data for Compounds 1–3<sup>a</sup>**

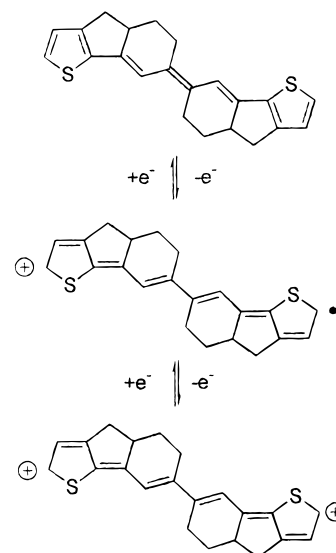
compd	$E_{p,a}^1$ (V)	$E_{p,a}^2$ (V)	$E_{p,a}^2 - E_{p,a}^1$ (mV)
<b>1</b>	0.95	1.25	300
<b>2</b>	0.51	0.80	290
<b>Z-3a</b>	0.65	0.90	250
<b>E-3a</b>	0.63	0.90	270
<b>3b</b>	0.66	0.95	290

<sup>a</sup> Conditions: ca.  $1 \times 10^{-3}$  M in  $1 \times 10^{-1}$  M  $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ ; scan rate  $100 \text{ mV s}^{-1}$ ; Pt electrodes; reference SCE.

shows that the potential difference  $E_{p,a}^2 - E_{p,a}^1$  related to the Coulombic repulsion between positive charges in the dication is relatively unaffected by rigidification and remains in the 250–300 mV range. This is rather surprising, since an increase in effective conjugation leads generally to a decrease or even canceling of  $E_{p,a}^2 - E_{p,a}^1$ .<sup>2b,10,19</sup> This unusual behavior, reminiscent of that of  $\pi$ -donors based on bridged dithienylethylene,<sup>20</sup> could be related to the geometrical changes resulting from the redox processes. In fact, oxidation to the cation radical state induces a transition from an aromatic to a quinoid thiophene ring with an inversion of bond length alternation leading to the flip of the median double bond (C11A–C11B in Figure 1) to a single one (Scheme 6). Since rotations around the central single bond become possible for both the bridged and the open-chain compounds, the difference between the two systems is much less in the cation radical than in the neutral state and the energy needed by the second oxidation step is comparatively less affected by the bridging of the molecule than that required by the first oxidation.<sup>20</sup>

**Optical Properties.** The electronic absorption spectra of compounds **Z-3a** and **E-3a** show a well-resolved vibronic fine structure. The ca. 0.18 eV difference between consecutive maxima is consistent with a coupling of the vibronic C=C stretching mode to the electronic structure.<sup>21</sup> The data in Table 3 show that rigidification produces a red shift of  $\lambda_{\text{max}}$ , indicative of an extension of effective conjugation. The largest red shift observed for **2** (30 nm) suggests, in agreement with CV data, that this compound is more planar than

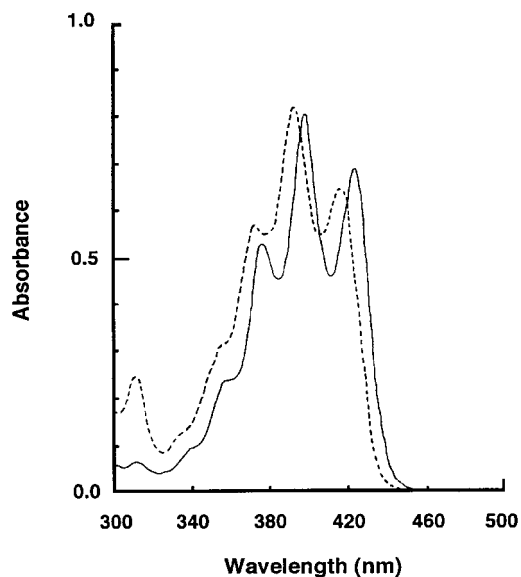
**Scheme 6**



**Table 3. UV–Visible and Fluorescence Spectroscopic Data for Dithienylhexatrienes in  $\text{CH}_2\text{Cl}_2$**

compd	$\lambda_{\text{max}}$ (nm)	$\log \epsilon$	$\Delta E^a$ (eV)	$\lambda_{\text{em}}^b$ (nm)	$\text{SS}^c$ (eV)	$\phi_{\text{em}}$
<b>1</b>	381	4.84	2.96	519	0.86	0.20
<b>2</b>	411	4.67	2.68	525	0.65	0.38
<b>Z-3a</b>	392	4.70	2.83	483	0.59	0.54
<b>E-3a</b>	398	4.84	2.81	471	0.48	0.70
<b>3b</b>	398	4.49	2.80	470	0.48	0.40

<sup>a</sup> Estimated from the long-wavelength absorption edge. <sup>b</sup> Maximum of the emission band. <sup>c</sup> Stokes shift between the maximum of the emission and absorption bands.



**Figure 3.** Electronic absorption spectra of **E-3a** (solid line) and **Z-3a** (dashed line) in  $\text{CH}_2\text{Cl}_2$ .

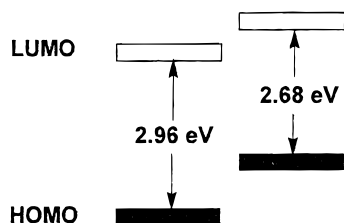
compounds **3**. As expected, **E-3a** absorbs at a longer wavelength than **Z-3a**. The *E* configuration postulated for **E-3a** is further confirmed by its higher  $\epsilon$  value and by the absence of the cis band,<sup>22</sup> which is clearly apparent at 312 nm in the spectrum of **Z-3a** (Figure 3). A further confirmation is provided by the red shift of  $\lambda_{\text{max}}$  from 392

(19) Roncali, J. *J. Mater. Chem.* **1997**, *12*, 2037.

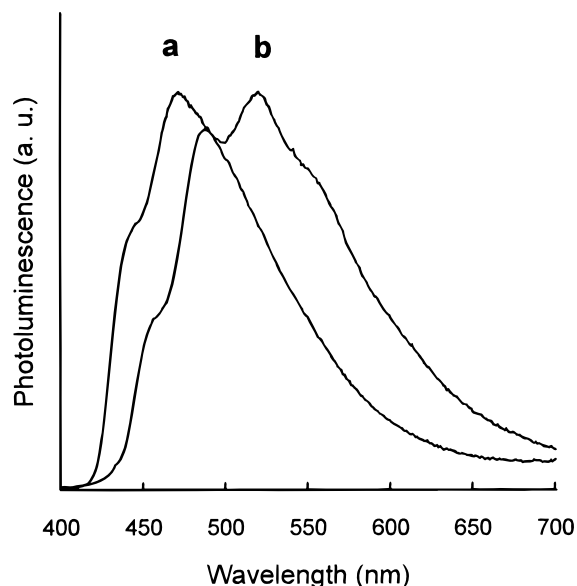
(20) Brisset, H.; Le Moustarder, S.; Blanchard, P.; Illien, B.; Riou, A.; Orduna, J.; Garin, J.; Roncali, J. *J. Mater. Chem.* **1997**, *7*, 2027.

(21) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci.* **1987**, *25*, 1071.

(22) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1967.



**Figure 4.** Schematic diagram of the MO levels in the unbridged (left) and bridged (right) dithienylhexatrienes.

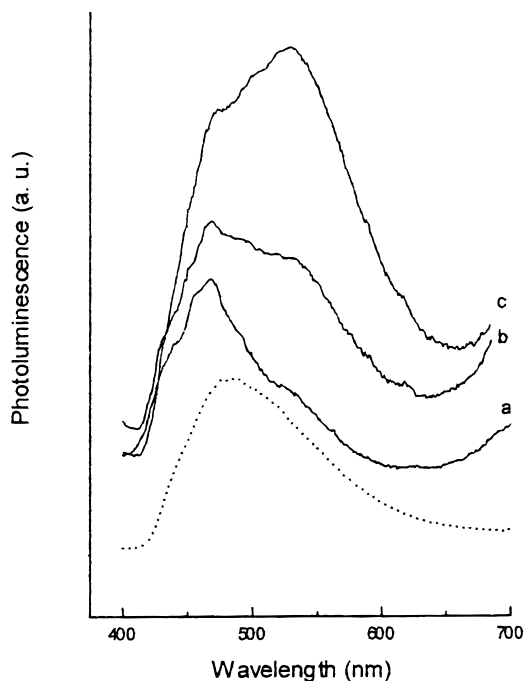


**Figure 5.** Normalized fluorescence emission spectra of **1** (b) and *E*-**3a** (a) in  $\text{CH}_2\text{Cl}_2$ .

to 398 nm and by the bleaching of the *cis* band caused by visible light irradiation of a  $\text{CH}_2\text{Cl}_2$  solution of *Z*-**3a**.

As shown in Table 3, rigidification of compound **1** leads to a significant reduction of the HOMO–LUMO gap ( $\Delta E$ ), up to 0.28 eV between **1** and **2**. However, this decrease is noticeably smaller than the 0.44 V negative shift of  $E_{p,a}^1$  (Table 2). Since  $E_{p,a}^1$  is related to the HOMO level,<sup>23</sup> these results imply that the bridging of the molecule simultaneously raises the HOMO and LUMO levels, the observed gap reduction resulting from a larger upshift of the HOMO (Figure 4).

Figure 5 shows the fluorescence emission spectra of compounds **1** and *E*-**3a**. The emission spectrum of **1** appears as the mirror image of the absorption spectrum and retains a well-resolved vibronic fine structure. In contrast, the resolution of the fine structure decreases for the bridged compounds and even completely vanishes for **2** (not shown). This behavior, which contrasts with that generally observed for luminescent conjugated oligomers or polymers,<sup>24</sup> suggests that the bridged molecules are less rigid in their first relaxed excited state. This phenomenon can be related to the specific structure of compounds **2** and **3**, in which transition from the aromatic ground state to a quinoid excited state leads to



**Figure 6.** Fluorescence emission spectra of PMMA films containing increasing concentrations of *Z*-**3a**: (a) optical density (OD) = 0.20; (b) OD = 0.35; (c) OD = 0.80. The emission spectrum in  $\text{CH}_2\text{Cl}_2$  solution (dotted line) is reported for comparison.

the formation of an essentially single bond in the middle part of the molecule, thus leading to a smaller rotational energy barrier in the excited state than in the ground state.

As shown in Table 3, all bridged fluorophores and especially the tricyclic compounds **3** exhibit much smaller Stokes shifts than **1**, indicating that rigidification of the molecule minimizes the nonradiative decay channel. Consequently, all bridged molecules exhibit a considerable enhancement of the fluorescence quantum yield ( $\phi_f$ ), which reaches for *E*-**3a** a value as high as 0.70, comparable to that of the most efficient conjugated systems.<sup>25</sup> Measurements on solutions of compounds *Z*-**3a** with optical densities ranging from 0.05 to 0.20 show no variation of  $\phi_f$ , which allows us to rule out aggregation phenomena in this concentration range.

To gain further information about the potential of compounds **3** for LED applications, the absorption and emission spectra of films cast from  $\text{CH}_2\text{Cl}_2$  solutions containing PMMA and various concentrations of compounds **1** and *Z*-**3a** have been recorded. While for compound **1** the films appear translucent due to the formation of microcrystals, films of good optical transparency were obtained for *Z*-**3a**. For compound **1** both the absorption and emission spectra were quite similar to the solution spectra. In contrast, while incorporation of compound *Z*-**3a** into a PMMA matrix does not change the absorption spectrum, a 20 nm blue shift of the maximum of the emission band occurs for the most dilute sample (Figure 6a). This leads to a decrease of the Stokes shift from 0.59 to 0.48 eV (Table 3). Increasing the substrate concentration in the film, and hence the optical density, induces a redistribution of the relative intensities of the

(23) (a) Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98. (b) Lyons, L. E. *Aust. J. Chem.* **1980**, *33*, 1717. (c) Loutfy, R. O.; Cheng, Y. C. *J. Chem. Phys.* **1980**, *73*, 2902.

(24) (a) Bäuerle, P. *Adv. Mater.* **1992**, *4*, 102. (b) Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. J. *J. Chem. Phys.* **1994**, *101*, 1673. (c) Belletête, M.; Mazerolle, L.; Desrosiers, N.; Leclerc, M.; Durocher, G. *Macromolecules* **1995**, *28*, 8587.

(25) (a) Stampfl, J.; Graupner, W.; Leising, G.; Scherf, U. *J. Lumin.* **1995**, *63*, 117. (b) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

emission subbands, leading to an apparent red shift of the emission maximum. While this latter phenomenon is probably related to the reabsorption of the emitted light caused by a overly high concentration of fluorophore in the film,<sup>26</sup> the blue shift observed for the dilute sample is more difficult to interpret. The Stokes shift is related to the work of reorientation of the solvent dipole under the influence of the changed dipole of the excited solute.<sup>27</sup> For a given change of the fluorophore dipole and a constant solvent dipole, this process is a function of viscosity because of the restriction of the rate of molecular movement.<sup>28</sup> Assuming comparable changes in dipole moment between the ground and excited states for both compounds, the decrease of the Stokes shift for **Z-3a** might reflect a more restricted mobility of the molecule in the PMMA matrix than for the open-chain compound **1**. In the frame of this hypothesis interactions of the two exocyclic bridges of **Z-3a** with PMMA would contribute to fasten the molecule in its polymeric environment. As far as it is confirmed, this reduced mobility could be particularly interesting for the synthesis of NLO-phores using compounds **3** as electron relays, since an improved long-term temporal stability of the aligned chromophore dipoles in the host matrix may be expected.

The thermal stability of the compounds has been analyzed by differential scanning calorimetry at a ramping rate of 10 °C/min under an ambient atmosphere. Compound **1** melts at 212–213 °C, in agreement with literature data,<sup>12b</sup> and starts to decompose at this temperature. Compound **Z-3a** shows a sharp melting point at 255 °C, while, due to the presence of two diastereomers, **E-3a** exhibits a broad peak extending from 275 to 305 °C with a maximum at 301 °C. For both **Z-3a** and **E-3a** no decomposition was observed even at the highest investigated temperature (340 °C). In addition to the obvious effect related to the raising of the melting point, this more than 100 °C increase in thermal stability resulting from the bridging may also be related to the restricted rotational disorder and to the substitution of ethylenic hydrogens that are thought to represent an important source of instability in stilbene-like systems.<sup>29</sup>

### Conclusion

New 1,6-dithienylhexa-1,3,5-trienes rigidified by multiple bridging of the polyenic system have been synthesized from precursor ketones prepared by Robinson annulation of cyclopenta[*b*]thiophen-6-ones. Rigidification of the  $\pi$ -conjugated system produces a significant enhancement of  $\pi$ -electron delocalization and thermal stability which, associated with a possible reduced mobility of these systems in rigid matrixes, make them highly interesting as electron relays for the synthesis of efficient and stable push–pull NLO-phores.

On the other hand, the strong enhancement of fluorescence quantum yield and thermal stability achieved by the multiple bridging of the conjugated system makes

this approach particularly attractive for the development of highly photoluminescent and thermally stable fluorophores potentially useful for LED application. Although achievement of quantum yields ranking among the highest reported for thiophene-based conjugated systems already represents an important result, thiophenic fluorophores are generally less emissive and stable than their benzenic analogues. On this basis, extension of the above strategy to the synthesis of new fluorophores based on the benzenic analogues of compounds **2** and **3** is now underway and will be reported in future publications.

### Experimental Section

Electrochemical experiments were carried out with a PAR 273 potentiostat–galvanostat in a three-electrode single-compartment cell equipped with a platinum microelectrode of  $7.85 \times 10^{-3}$  cm<sup>2</sup> area, a platinum-wire counter electrode, and a saturated calomel reference electrode (SCE). UV–vis absorption spectra were recorded on a Lambda 2 Perkin-Elmer spectrometer. Fluorescence emission spectra were recorded on a PTI Quanta Master 1 spectrofluorimeter. Absolute quantum yields were determined in dichloromethane at 25 ± 0.1 °C, using anthracene as standard (Fluka puriss for scintillation, sublimed twice before use) ( $\phi = 0.27$  in 95% EtOH).<sup>30</sup> Solutions were degassed by argon bubbling, and optical densities were adjusted below 0.10. Dichloromethane (HPLC grade) and 95% EtOH (spectrophotometric grade) were used as received. PMMA films were cast on glass from chloroform solutions containing 30 g L<sup>-1</sup> PMMA medium MW (Aldrich) and  $1 \times 10^{-3}$  mol L<sup>-1</sup> of substrate.

**Robinson Annulation of Compound 4a.** A solution of ketone **4a** (1.52 g, 11 mmol) in anhydrous methanol (50 mL) in the presence of KOH (0.11 g, 1.96 mmol) was refluxed for 20 min, cooled to room temperature before the dropwise addition of MVK (0.97 mL, 11.6 mmol), and then refluxed again for 17 h. At room temperature, after the successive additions of water (30 mL) and a 1 M aqueous solution of HCl (30 mL), the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with water (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated in vacuo. The residue was chromatographed (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/AcOEt, initial ratio 95:5 and progressive addition of AcOEt to 80:20). Four fractions of different *R<sub>f</sub>* (CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 85:15) were separated: F1 (0.68 g, *R<sub>f</sub>* 0.92), F2 (0.25 g, *R<sub>f</sub>* 0.78), F3 (0.32 g, *R<sub>f</sub>* 0.54), F4 (0.43 g, *R<sub>f</sub>* 0.26). The first one corresponded to unreacted **4a** (45% recovered), the second one contained compound **5** among other products, and the third one contained essentially a diastereomeric form of the spiro alcohol **6** (10%). The last fraction, F4, contained a mixture of another diastereomeric form of **6** and the alcohol **7a**, this latter compound being identified with a pure sample obtained via a different route (see below).

**Thieno[3',2':8,9]bicyclo[4.3.0]non-1(2)-en-3-one (5).** Among the three different spots observed in TLC for the fraction F2 (Et<sub>2</sub>O/petroleum ether (PE) 7:3), the second one, with an *R<sub>f</sub>* value of 0.39, corresponded to the expected product. Chromatography of F2 (silica gel, Et<sub>2</sub>O/PE, 6:4) gave 60 mg (3%) of white solid which gave suitable crystals for X-ray determination after slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/EtOH solution. Mp: 135 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.93 (m, 1H), 2.32 (m, 1H), 2.41 (m, 1H), 2.57 (m, 1H), 2.60 (dd, 1H, <sup>2</sup>*J*<sub>gem</sub> = 16.2 Hz, <sup>3</sup>*J* = 5.0 Hz), 3.14 (dd, 1H, <sup>2</sup>*J*<sub>gem</sub> = 16.2 Hz, <sup>3</sup>*J* = 7.3 Hz), 3.50 (m, 1H), 5.97 (d, 1H, <sup>4</sup>*J* = 2.2 Hz), 6.96 (d, 1H, <sup>3</sup>*J* = 4.9 Hz), 7.57 (d, 1H, <sup>3</sup>*J* = 4.9 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  29.36, 33.85, 37.91, 47.18, 115.29, 123.34, 135.47, 140.27, 157.74, 163.78, 199.00. MS (EI): *m/z* (*I*, %) = 190 (M<sup>+</sup>, 83), 162 (100), 134 (79). HRMS: calcd for C<sub>11</sub>H<sub>10</sub>OS 190.0452, found 190.0456. IR (KBr): 1688 and 1641 (C=O), 1614 (C=C) cm<sup>-1</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ) 317 (25 100).

**Spiro(2-acetyl-1-hydroxy-1-methyl-cyclohexane)-4,5'-(4,5-dihydro-6H-cyclopenta[*b*]thiophen-6-one) (6).** Col-

(26) (a) Budo, A.; Ketskemety, I. *J. Chem. Phys.* **1956**, *25*, 595. (b) Batchelder, J. S.; Zewail, A. H.; Cole, T. *Appl. Opt.* **1979**, *18*, 3090. (c) Roncali, J.; Garnier, F. *Appl. Opt.* **1984**, *23*, 2809.

(27) (a) Sambursky, S.; Wolsohn, G. *Trans. Faraday Soc.* **1940**, *36*, A27. (b) Hercules, D. M.; Rodgers, L. B. *J. Chem. Phys.* **1960**, *64*, 397. (c) Lippert, E. *Angew. Chem.* **1961**, *73*, 695.

(28) Gilmore, E. H.; Gibson, G. E.; McClure, D. S. *J. Chem. Phys.* **1952**, *20*, 829.

(29) (a) Lyle, T. A.; Daub, G. H. *J. Org. Chem.* **1979**, *44*, 4933. (b) Lux, A.; Holmes, A. B.; Cervini, R.; Davies, J. E.; Morati, S. C.; Grüner, J.; Cacialli, F.; Friend, R. H. *Synth. Met.* **1997**, *84*, 293.

(30) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.



orless oil. MS (EI):  $m/z$  ( $I, \%$ ) 278 ( $M^+$ , 5), 260 (15), 218 (30), 208 (100), 151 (97), 150 (33) 138 (35). UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) 265.

**Spiro[2-acetyl-1-methyl-cyclohex-1-ene]-4,5'-(4,5-dihydro-6H-cyclopenta[*b*]thiophen-6-one) (8).** Complete identification of **6** was achieved after a dehydration reaction leading to compound **8**. The colorless oil **F3** (0.32 g, 1.15 mmol) was dissolved in anhydrous benzene (20 mL). After addition of *p*-toluenesulfonic acid (5 mg) and molecular sieves (4 Å), the mixture was refluxed for 48 h and cooled to room temperature. After addition of water (20 mL), the mixture was extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated in vacuo. Chromatography of the residue (silica gel,  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ , 95:5) gave 0.16 g (54%) of yellow oil, which slowly solidifies. Mp: 100–102 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.59 (m, 1H,  $^2J_{\text{gem}} = 13.3$  Hz), 1.92 (m, 1H,  $^2J_{\text{gem}} = 13.3$  Hz and  $^3J = 9.1$  Hz), 1.92 (s, 3H), 2.15 (br d, 1H,  $^2J_{\text{gem}} = 16.6$  Hz), 2.19 (s, 3H), 2.30 (m, 2H), 2.69 (m, 1H,  $^2J_{\text{gem}} = 16.6$  Hz,  $^4J = 2.5$  Hz), 2.75 (d, 1H,  $^2J_{\text{gem}} = 17.3$  Hz), 2.86 (d, 1H,  $^2J_{\text{gem}} = 17.3$  Hz), 7.00 (d, 1H,  $^3J = 4.8$  Hz), 7.92 (d, 1H,  $^3J = 4.8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.22, 28.76, 29.69, 30.91, 35.65, 36.47, 54.22, 124.07, 131.19, 139.21, 140.31, 141.13, 165.95, 200.87, 203.13. MS (EI):  $m/z$  ( $I, \%$ ) 260 ( $M^+$ , 22), 217 (100), 125 (32), 43 (56). IR (KBr): 1695 sh and 1678 ( $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) 260. Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{S}$ : C, 69.20; H, 6.19; O, 12.29; S, 12.31. Found: C, 69.16; H, 6.16; O, 12.59; S, 12.21.

**Compound 9a via the Alcohol 7a.** A mixture of ketone **4a** (2 g, 14.5 mmol) and KOH (1.57 g, 28.00 mmol) in anhydrous methanol (85 mL) was refluxed for 1 h before addition in one portion of MVK (2.50 mL, 30.53 mmol). Reflux was continued for 15 h, and the mixture was cooled to room temperature. After addition of water, the mixture was neutralized by 4 M aqueous HCl and diluted with  $\text{CH}_2\text{Cl}_2$ . The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with water, dried ( $\text{MgSO}_4$ ), and evaporated in vacuo. Chromatography of the residue (silica gel, first  $\text{CH}_2\text{Cl}_2$  then  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  (1:1)) allowed us to isolate a fraction corresponding to the alcohol **7a** (2.55 g,  $R_f$  0.34). The latter was dissolved in anhydrous toluene (50 mL), and the resulting solution was refluxed before addition of concentrated  $\text{H}_2\text{SO}_4$  (0.5 mL). The mixture was refluxed again for 1 h and then cooled to room temperature. After successive additions of water and an aqueous saturated solution of  $\text{Na}_2\text{CO}_3$ , the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The black residue that stuck to the reaction flask, which contained some good product, was dissolved in THF. The organic phases were gathered, washed with water, dried ( $\text{MgSO}_4$ ), and evaporated in vacuo. Chromatography of the crude product (silica gel,  $\text{CH}_2\text{Cl}_2$ ) afforded 0.98 g (28%) of pale yellow powder. Recrystallization in 1:1  $\text{CH}_2\text{Cl}_2/\text{EtOH}$  gave 0.63 g of beige crystals. A second crop of 0.135 g was obtained after evaporation of the mother liquor and further recrystallization to finally yield 0.765 g (22%) of the target compound. Mp: 183 °C.

**9-Hydroxy-9-methyl-thieno[3',2':3,4]tricyclo[6.3.1.0<sup>1,5</sup>]-dodeca-5(6)-en-7-one (7a; two Diastereomers (70:30)).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.25 (s,  $\text{CH}_3$ , 1st dia), 1.41 (s,  $\text{CH}_3$ , 2nd dia), 1.43–1.70 (m, 2H), 1.75–1.90 (m, 1H), 2.05–2.30 (m, 2H), 2.38–2.55 (m, 2H), 2.62–2.85 (m, 2H), 5.96 (s, 1H, 1st dia), 6.08 (s, 1H, 2nd dia), 6.91 (d, 1H,  $^3J = 4.7$  Hz, 1st dia), 6.93 (d, 1H,  $^3J = 4.9$  Hz, 2nd dia), 7.54 (d, 1H,  $^3J = 4.7$  Hz, 1st dia), 7.58 (d, 1H,  $^3J = 4.9$  Hz, 2nd dia).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25.74, 29.10, 31.21, 33.07, 34.02, 34.39, 35.63, 36.91, 41.57, 42.06, 50.50, 50.74, 54.65, 55.77, 67.68, 68.55, 116.49, 116.78, 123.68, 123.72, 135.42, 136.07, 138.87, 139.01, 156.74, 156.81, 164.00, 165.02, 200.36, 201.61. MS (EI):  $m/z$  ( $I, \%$ ) 260 ( $M^+$ , 31), 190 (100), 175 (18), 147 (19), 115 (11). IR (KBr): 3392 ( $\text{O}-\text{H}$ ), 1650–1607 (br band  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) 324.

**9-Methyl-thieno[3',2':3,4]tricyclo[6.3.1.0<sup>1,5</sup>]-dodeca-5(6),9-(10)-dien-7-one (9a).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.78 (m, 3H,  $^4J = 1.4$  Hz,  $^5J = 2.2$  Hz,  $^5J = 1.4$  Hz), 2.25 (dd, 1H,  $^2J_{\text{gem}} = 12$  Hz,  $^3J = 2.8$  Hz), 2.34 (m, 1H,  $^2J_{\text{gem}} = 18.5$  Hz,  $^3J = 4.4$  Hz,  $^5J = 1.4$  Hz), 2.39 (dd, 1H,  $^2J_{\text{gem}} = 12$  Hz,  $^3J = 2.8$  Hz), 2.45 (m, 1H,  $^2J_{\text{gem}} = 18.5$  Hz,  $^3J = 2.7$  Hz,  $^5J = 2.2$  Hz), 2.81 (d, 1H,

$^2J_{\text{gem}} = 15.9$  Hz), 2.86 (dd, 1H,  $^3J = 2.8$  Hz,  $^3J = 2.8$  Hz), 2.97 (d, 1H,  $^2J_{\text{gem}} = 15.9$  Hz), 5.39 (m, 1H,  $^3J = 4.4$  Hz,  $^3J = 2.7$  Hz,  $^4J = 1.4$  Hz), 5.83 (s, 1H), 6.96 (d, 1H,  $^3J = 4.8$  Hz), 7.54 (d, 1H,  $^3J = 4.8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.67, 36.42, 37.84, 43.01, 48.94, 49.89, 113.84, 121.02, 123.45, 131.90, 134.67, 139.51, 154.84, 163.78, 198.05. MS (EI):  $m/z$  ( $I, \%$ ) 242 ( $M^+$ , 100), 227 (24), 214 (24), 199 (32), 161 (51). IR (KBr): 1650 ( $\text{C}=\text{O}$ ), 1607 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ) 325 (21 000).

**Compound 9b via 7b.** A mixture of ketone **4b** (0.8 g, 4.12 mmol) and KOH (0.2 g, 3.57 mmol) in anhydrous methanol (10 mL) was refluxed for 0.5 h before addition in one portion of MVK (0.71 mL, 8.67 mmol). Reflux was continued for 15 h, and the mixture was cooled to room temperature. After addition of water, the mixture was neutralized by 4 M aqueous HCl and diluted with  $\text{CH}_2\text{Cl}_2$ . The aqueous phase was separated by decantation and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with water, dried ( $\text{MgSO}_4$ ), and evaporated in vacuo. Chromatography of the residue (silica gel,  $\text{Et}_2\text{O}/\text{PE}$  8:2) gave a first fraction ( $R_f > 0.4$ ) containing unreacted starting material and other byproducts, while the following fractions corresponding to the various diastereomers of alcohol **7b** were collected, affording 0.38 g of a yellow-brown oil. The latter was dissolved in anhydrous toluene (30 mL), and the resulting solution was refluxed before addition of concentrated  $\text{H}_2\text{SO}_4$  (0.25 mL). The reaction mixture was refluxed for 1.5 h and then cooled to room temperature. After successive addition of water and aqueous  $\text{Na}_2\text{CO}_3$ , the mixture was extracted with  $\text{Et}_2\text{O}$ . The brown residue that stuck to the reaction flask, which contained some good product, was dissolved in THF (30 mL). The organic phases were gathered, washed with water, dried ( $\text{MgSO}_4$ ), and evaporated in vacuo. The crude product was chromatographed (silica gel,  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  95:5), affording 0.18 g (15%) of **9b** as a yellow oil which contained two diastereomers, as evidenced by TLC ( $\text{PE}/\text{Et}_2\text{O}$  9:1).

**2-Butyl-9-hydroxy-9-methylthieno[3',2':3,4]tricyclo[6.3.1.0<sup>1,5</sup>]-dodeca-5(6)-en-7-one (7b).** UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) 326. IR (NaCl): 3418 ( $\text{O}-\text{H}$ ), 1707 and 1654 ( $\text{C}=\text{O}$ ), 1610 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

**2-Butyl-9-methyl-thieno[3',2':3,4]tricyclo[6.3.1.0<sup>1,5</sup>]-dodeca-5(6),9(10)-dien-7-one (9b).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.89 (t, 3H,  $^3J = 6.3$  Hz), 1.15–1.60 (m, 5H), 1.63–1.80 (m, 4H), 2.03 (dd, 1H,  $^2J_{\text{gem}} = 12$  Hz and  $^3J = 3.1$  Hz), 2.12–2.62 (m, 3H), 2.75–2.93 (m, 2H), 5.30–5.45 (m, 1H), 5.83 (s, 1H), 6.97 (d, 1H,  $^3J = 4.7$  Hz), 7.50 (d, 1H,  $^3J = 4.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  13.97, 21.56, 22.71, 29.74, 31.79, 32.23, 39.29, 49.49, 51.69, 52.68, 114.02, 121.55, 124.21, 132.05, 133.84, 138.79, 159.87, 163.11, 198.54. MS (EI):  $m/z$  ( $I, \%$ ) 298 ( $M^+$ , 100), 241 (73), 217 (52), 147 (41). IR (KBr): 1656 ( $\text{C}=\text{O}$ ), 1615 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ) 326 (15 600).

**Robinson Annulation of Compound 4c.** A mixture of ketone **4c** (0.36 g, 2.37 mmol), KOH and (0.20 g, 3.57 mmol) in anhydrous methanol (15 mL) was refluxed for 15 min. At room temperature, MVK (0.22 mL, 2.64 mmol) was added and the mixture was refluxed for 1 h and then cooled to room temperature. After addition of water and 1 M aqueous HCl, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated in vacuo. Chromatography (silica gel,  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ , 95:5) gave two fractions ( $R_f$  0.46 and 0.12). The second one corresponded to the alcohol **12** (0.05 g, 10%), while the first one was again chromatographed (silica gel,  $\text{Et}_2\text{O}/\text{PE}$  45:55) to separate two new fractions. The first one contained essentially the expected ketone **10** (0.06 g, 12%) and the second one the diketone **11** (0.28 g, 53%).

**6-Methylthieno[3',2':8,9]bicyclo[4.3.0]non-1(2)-en-3-one (10).** Pale yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.40 (s, 3H), 2.10–2.20 (m, 2H), 2.48 (m, 1H,  $^2J_{\text{gem}} = 18.1$  Hz,  $^3J = 4.5$  Hz,  $^3J = 2$  Hz), 2.60 (m, 1H,  $^2J_{\text{gem}} = 18.1$  Hz,  $^3J = 12$  Hz,  $^3J = 6.4$  Hz), 2.77 (d, 1H,  $^2J_{\text{gem}} = 16.4$  Hz), 2.79 (d, 1H,  $^2J_{\text{gem}} = 16.4$  Hz), 5.93 (s, 1H), 6.96 (d, 1H,  $^3J = 4.8$  Hz), 7.58 (d, 1H,  $^3J = 4.8$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  26.46, 34.00, 34.56, 43.25, 49.31, 115.14, 123.70, 135.46, 139.40, 155.93, 167.70, 198.47. MS (EI):  $m/z$  ( $I, \%$ ) 204 ( $M^+$ , 58), 176 (100), 148 (66), 147 (66).

HRMS: calcd for  $C_{12}H_{12}OS$  204.0609, found 204.0609. IR (NaCl): 1690 and 1652 (C=O), 1617 (C=C)  $cm^{-1}$ . UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (nm) ( $\epsilon$ ) 319 (22 400). Anal. Calcd for  $C_{12}H_{12}OS$ : C, 70.55; H, 5.92; O, 7.83; S, 15.69. Found: C, 70.79; H, 5.97; O, 8.13; S, 15.24.

**4,5-Dihydro-5-(2-butanon-4-yl)-5-methyl-6H-cyclopenta[b]thiophen-6-one (11).** Yellow oil.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.28 (s, 3H), 1.91 (m, 2H), 2.10 (s, 3H), 2.39 (t, 2H,  $^3J = 8.1$  Hz), 2.79 (d, 1H,  $^2J_{gem} = 17.4$  Hz), 2.91 (d, 1H,  $^2J_{gem} = 17.4$  Hz), 7.02 (d, 1H,  $^3J = 4.8$  Hz), 7.92 (d, 1H,  $^3J = 4.8$  Hz).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  24.25, 29.92, 32.05, 38.12, 38.71, 54.15, 123.94, 139.51, 141.03, 165.65, 201.32, 208.20. MS (EI):  $m/z$  ( $I$ , %) 222 ( $M^+$ , 38), 152 (100), 151 (45), 43 (49). HRMS: calcd for  $C_{12}H_{14}O_2S$  222.0714, found: 222.0709. IR (NaCl): 1710 sh and 1687 (C=O)  $cm^{-1}$ . UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (nm) 265. Anal. Calcd for  $C_{12}H_{14}O_2S$ : C, 64.84; H, 6.35; O, 14.39; S, 14.42. Found: C, 64.87; H, 6.26; O, 14.54; S, 14.31.

**6-Hydroxy-1,6-dimethylthieno[2',3':3,4]bicyclo[3.3.0]octan-2-one (12).** Colorless oil; mixture of the two different diastereomers.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.36 and 1.38 (2s, 3H), 1.44 and 1.51 (2s, 3H), 1.53–1.68 (m, 1H), 1.69–1.80 (m, 1H), 1.89–2.02 (m, 1H), 2.05–2.15 (m, 1H), 3.01 and 3.09 (2s, 1H), 7.08 and 7.16 (2d, 1H,  $^3J = 4.7$  Hz), 7.92 and 7.96 (2d, 1H,  $^3J = 4.7$  Hz). MS (EI):  $m/z$  ( $I$ , %) 222 ( $M^+$ , 60), 152 (100). IR (NaCl): 3439 (O–H), 1686 (C=O)  $cm^{-1}$ . UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (nm) 267.

**1,6-Dimethylthieno[2',3':3,4]bicyclo[3.3.0]oct-6(7)-en-2-one (13).** A mixture of the alcohol **12** (0.16 g, 0.72 mmol), *p*-toluenesulfonic acid (3 mg) in anhydrous benzene (20 mL) was refluxed 24 h using a Dean–Stark apparatus. At room temperature, the reaction mixture was diluted with  $Et_2O$ , and the resulting solution was washed with water, dried ( $Na_2SO_4$ ), and evaporated in vacuo. Chromatography (silica gel,  $CH_2Cl_2$ ) gave ketone **13** (0.08 g, 55%) as a yellow oil.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.44 (s, 3H), 1.83 (br s, 3H), 2.31 (m, 1H,  $^2J_{gem} = 17.5$  Hz,  $^3J = 5$  Hz,  $^5J = 2.4$  Hz), 2.73 (m, 1H,  $^2J_{gem} = 17.5$  Hz,  $^3J = 5$  Hz and  $^5J = 2.4$  Hz), 3.66 (s, 1H), 5.19 (br s, 1H), 7.09 (d, 1H,  $^3J = 4.8$  Hz), 7.91 (d, 1H,  $^3J = 4.8$  Hz).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  15.46, 23.69, 41.96, 60.87, 62.23, 123.25, 124.48, 138.50, 138.88, 140.76, 169.07, 202.12. MS (EI):  $m/z$  ( $I$ , %) 204 ( $M^+$ , 100), 189 (47), 161 (56). HRMS: calcd for  $C_{12}H_{12}OS$  204.0609, found 204.0602. IR (KBr): 1691 (C=O)  $cm^{-1}$ . UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (nm) 268. Anal. Calcd for  $C_{12}H_{12}OS$ : C, 70.55; H, 5.92; S, 15.69. Found: C, 70.49; H, 6.03; S, 15.62.

**Compounds 10 and 12 from Diketone 11.** Diketone **11** (0.4 g, 1.80 mmol) was dissolved in a NaOEt (1.5 equiv)/ $EtOH$  solution, which was first prepared by addition of 62 mg of Na (2.70 mmol) in anhydrous  $EtOH$  (20 mL). The mixture was refluxed for 1 h and cooled to room temperature before addition of water and 3 M aqueous HCl. After extraction with  $Et_2O$ , the organic phase was washed with water, dried ( $Na_2SO_4$ ), and evaporated in vacuo to give a brown oil containing two main products. Chromatography (silica gel ( $Et_2O/PE$  1:1)) gave 0.20 g (54%) of compound **10** and 0.08 g (20%) of alcohol **12**.

**Bis(9-methylthieno[3',2':3,4]tricyclo[6.3.1.0<sup>4,5</sup>]dodeca-5(6),9(10)-dien-7-ylidene) (3a).** After dropwise addition of  $TiCl_4$  (0.45 mL, 4.13 mmol) to 15 mL of anhydrous THF at 0 °C under an  $N_2$  atmosphere, zinc dust (0.54 g, 8.26 mmol) was added in one portion. The mixture was refluxed for 0.5 h and cooled to 0 °C. A solution of ketone **9a** (0.47 g, 1.94 mmol) in THF (40 mL) was added dropwise, and the mixture was refluxed again for 0.5 h. After it was cooled to room temperature and water was added, the mixture was extracted with  $CH_2Cl_2$ . The organic phase was washed with water, dried ( $MgSO_4$ ), and evaporated in vacuo. After two successive elutions, a TLC analysis ( $PE/CH_2Cl_2$  8:2) revealed the presence of three products. The residue was chromatographed (silica gel,  $PE/CH_2Cl_2$  9:1). Two different fractions, F1 and F2 (0.13 and 0.26 g respectively), were isolated as yellow powders corresponding to different diastereomers in 89% overall yield.

Recrystallization of F1 (Tol/PE) gave yellow needles (mp = 275–305 °C, with peak maximum at 294 °C). Recrystallization of F2 in  $PE-CH_2Cl_2$  gave 0.17 g of a pure diastereomer. Yellow-brown crystals (mp = 255 °C) of good quality were obtained for X-ray determination. Fraction F1 (**E-3a**):  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.65–1.80 (m, 6H), 1.85–1.95 (m, 2H), 2.10–2.18 (m, 2H), 2.25 (d, 2H,  $^2J_{gem} = 17.3$  Hz), 2.33 (d, 2H,  $^2J_{gem} = 17.3$  Hz), 2.65–2.85 (m, 4H), 3.50–3.65 (s, 2H), 5.20–5.35 (m, 2H), 6.62–6.68 (m, 2H), 6.83–6.91 (m, 2H), 7.15–7.25 (m, 2H); UV-vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (nm) ( $\epsilon$ ) 424 (58 900), 398 (69 000), 377 (45 300). Fraction F2 (**Z-3a**):  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.72 (d, 6H,  $^4J = 1.4$  Hz), 1.96 (dd, 2H,  $^2J_{gem} = 11.5$  Hz,  $^3J = 1.7$  Hz), 2.17 (dd, 2H,  $^2J_{gem} = 11.5$  Hz,  $^3J = 3.8$  Hz), 2.25 (d, 2H,  $^2J_{gem} = 17.3$  Hz), 2.33 (d, 2H,  $^2J_{gem} = 17.3$  Hz), 2.73 (d, 2H,  $^2J_{gem} = 15$  Hz), 2.82 (d, 2H,  $^2J_{gem} = 15$  Hz), 3.61 (br s, 2H), 5.28 (br s, 2H), 6.65 (s, 2H), 6.87 (d, 2H,  $^3J = 4.7$  Hz), 7.24 (d, 2H,  $^3J = 4.7$  Hz).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  21.63, 36.08, 38.41, 39.14, 42.67, 48.20, 113.42, 120.07, 123.10, 128.42, 132.15, 135.68, 142.14, 143.96, 148.87. MS (EI):  $m/z$  ( $I$ , %) 452 ( $M^+$ , 100), 226 (11). UV-vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (nm) ( $\epsilon$ ) 415 (40 600), 392 (50 600), 372 (36 200). Anal. Calcd for  $C_{30}H_{28}S_2$ : C, 79.60; H, 6.23. Found: C, 78.96; H, 6.26.

**Bis(2-butyl-9-methylthieno[3',2':3,4]tricyclo[6.3.1.0<sup>4,5</sup>]dodeca-5(6),9(10)-dien-7-ylidene) (3b).** This compound was prepared according to the procedure described for **3a** from  $TiCl_4$  (0.15 mL, 1.36 mmol), zinc dust (0.18 g, 2.75 mmol), and ketone **9b** (0.2 g, 0.67 mmol). After the usual workup a TLC analysis ( $PE/CH_2Cl_2$  9:1) revealed the presence of four different products. The residue was chromatographed on silica gel (cyclohexane/ $CH_2Cl_2$  1:1), affording 90 mg (48%) of a yellow oil corresponding to a mixture of all possible diastereomers.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.85–0.92 (m, 6H), 1.20–1.42 (m, 8H), 1.45–1.64 (m, 4H), 1.65–1.80 (m, 6H), 1.85–2.05 (m, 4H), 2.10–2.40 (m, 4H), 2.65–2.85 (m, 2H), 3.50–3.70 (m, 2H), 5.20–5.40 (m, 2H), 6.60–6.75 (m, 2H), 6.85–7.05 (m, 2H), 7.12–7.25 (m, 2H). MS (EI):  $m/z$  ( $I$ , %) 564 ( $M^+$ , 100), 507 (6), 282 (6). HRMS: calcd for  $C_{38}H_{44}S_2$  564.28845, found 564.2872. UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (nm) ( $\epsilon$ ) 420 (26 400), 398 (31 100), 379 (22 900). Anal. Calcd for  $C_{38}H_{44}S_2$ : C, 80.29; H, 8.18; S, 10.13. Found: C, 80.80; H, 7.85; S, 11.35.

**Bis(6-methylthieno[3',2':3,9]bicyclo[4.3.0]non-1(2)-en-3-ylidene) (2).** This compound was prepared according to the procedure described for **3a** (except for addition of ketone **10** at 0 °C and no reflux), from  $TiCl_4$  (0.31 mL, 2.80 mmol), zinc dust (0.37 g, 5.61 mmol), and ketone **10** (0.26 g, 1.27 mmol). After the usual workup the residue was filtered on silica gel ( $CH_2Cl_2$ ) and chromatographed (silica gel,  $CH_2Cl_2$ /cyclohexane 1:9). For solubility reasons the product was adsorbed on silica gel and then deposited on top of the column before elution. Compound **3** was finally obtained as a yellow solid (0.20 g, 84%) corresponding to different diastereomers. Mp: 198–230 °C.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.22, 1.24, and 1.26 (3s, 6H,  $CH_3$ ), 1.74–1.81 (m, 2H), 1.96–2.00 (m, 2H), 2.50–2.55 (m, 2H), 2.68–2.72 (m, 4H), 2.79–2.83 (m, 2H), 6.48, 6.53, 6.68, and 6.71 (4s, 2H), 6.85 (d, 2H,  $^3J = 4.7$  Hz), 7.23–7.26 (m, 2H). MS (EI):  $m/z$  ( $I$ , %) 376 ( $M^+$ , 100), 361 (22). HRMS: calcd for  $C_{24}H_{24}S_2$  376.1319, found 376.1319. UV-vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (nm) ( $\epsilon$ ) 432 (38 700), 411 (47 300), 390 (sh, 34 200). Anal. Calcd for  $C_{24}H_{24}S_2$ : C, 76.55; H, 6.42. Found: C, 76.45; H, 6.62.

**Supporting Information Available:** Tables giving positional and thermal parameters and bond distances and angles for **3a**, **5**, and **9a**, (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.