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# Aza-analogues of extended tetrathiafulvalenes

Raquel Andreu,[a] Javier Garín,[a,*] Carolina López,[a] Jesús Orduna[a] and Eric Levillain[b]

[a]*Departamento de Química Orgánica, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain*
[b]*Laboratoire CIMMA, CNRS UMR 6200. 2, Bd. Lavoisier, 49045 Angers Cedex, France*

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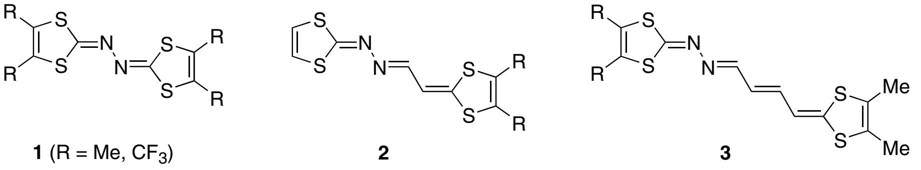
Dedicated to the memory of Dr. Juan Carlos del Amo, victim of terrorism (Madrid, 11 March 2004)

**Abstract**—The phosphoramidate-like reaction of 1,3-dithiole derived *N*-(diethoxyphosphinyl)hydrazones with formyl derivatives of 1,3-dithiole affords the longest aza-analogues of extended tetrathiafulvalenes with a polyenic spacer reported to date. Their structural and electrochemical properties are discussed.

Extended tetrathiafulvalenes have attracted much attention due to their low oxidation potentials when compared to simple tetrathiafulvalene (TTF) derivatives; in fact, the larger extension of the π-framework in the former allows not only the easy generation of the cation radical state, but also that of di- and higher polycationic states, due to the decreased on site Coulomb repulsions. To that end, a wealth of π-spacers, like polyenes, aromatic and heteroaromatic moieties have been used to connect the two dithiolylidene fragments.[1–4] On the other hand, the incorporation of nitrogen atoms instead of carbon atoms in the conjugated spacer has much less precedent in the literature. Thus, only two examples of symmetrical azine derivatives of general structure **1** have been reported to date,[5,6] along with a few 1,3-dithiol-2-ylidenehydrazino derivatives.[5,7–10]



**a**: R = H; **b**: R = Me

In this letter we describe the synthesis, characterization and electrochemical properties of the first aza-analogues of extended TTFs incorporating a polyenic chain of four or six conjugated atoms between the dithiole rings (**2** and **3**, respectively).

These compounds are unsymmetrical azines and can, therefore, show a tendency to disproportionate, so that a possible route to the target compounds making use of the reaction of dithiolium cations with hydrazine hydrate and further reaction of the resulting hydrazones with carbonyl compounds was ruled out. Among the different published procedures for the synthesis of unsymmetrical azines, the use of *N*-(diethoxyphosphinyl)-hydrazones looked promising,[11,12] provided that the necessary starting compounds **5** could be prepared. This turned out to be the case, and the reaction of diethyl phosphorohydrazidate[13] with dithiolium cations **4** under similar conditions to those previously reported by our group[10] afforded the first diethoxyphosphinylhydrazones in dithiole series (**5**)[14] (Scheme 1).

The reaction of **5a** with aldehydes **6**[15] did not proceed at room temperature, a fact, which can be ascribed to the

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* Corresponding author. Tel./fax: +34 976 761194; e-mail: jgarin@unizar.es

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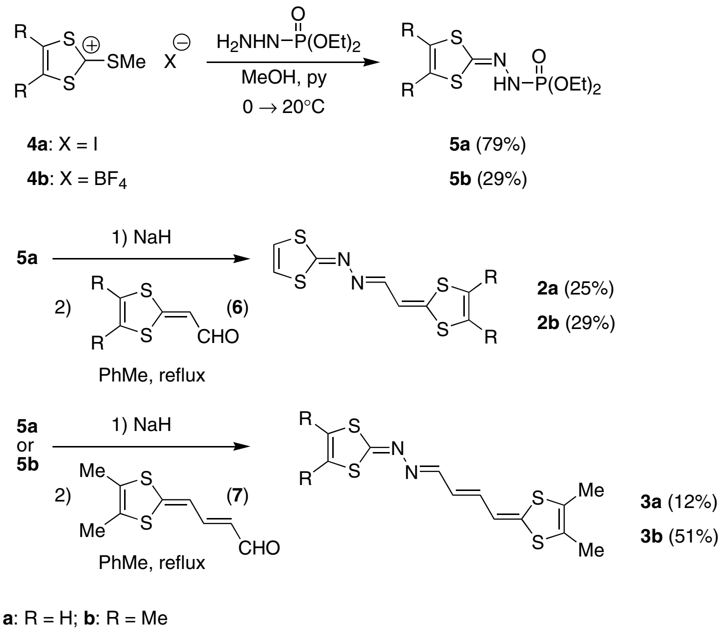


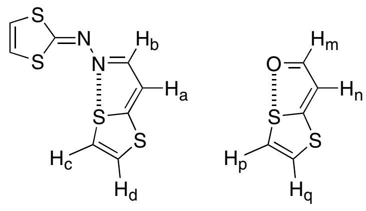
**Scheme 1.**

low electrophilicity of the carbonyl group of **6**, but led to azines **2** in refluxing toluene.[16] In a similar vein, azines **3**[17] were obtained from **5** and aldehyde **7**.[18]

$^1$H NMR spectroscopy shows that azines **2** adopt an *s-cis* conformation (Fig. 1), as revealed by the value of the coupling constants ($J_{ab}$ = 5.6 Hz for **2a** and 5.7 Hz for **2b**), which are very close to the one reported (4.9 Hz) for a related cyanoimino derivative whose structure has been determined by X-ray diffraction studies.[19,20]

The stabilizing 1,5 S–N interaction is responsible for this conformational preference.[10,19] Moreover, a long-range coupling between $H_a$ and $H_c$ ($J_{ac}$ = 1.5 Hz) is observed, but not between $H_a$ and $H_d$. This is in agreement with previous reports on some 6-substituted 1,4-dithiafulvenes.[21,22]

These features are also present in the $^1$H NMR spectrum ($CDCl_3$) of **6a**, which in our hands, is different from that previously described.[15] Thus, the formyl group adopts an *s-cis* conformation ($J_{mn}$ = 1.9 Hz), but there exists a coupling between the more distant hydrogen atoms of the dithiafulvene moiety ($J_{np}$ = 1.5 Hz, $J_{nq}$ = 0 Hz), and the two ring protons ($H_p$ and $H_q$) are not equivalent.[23]

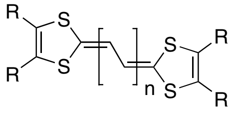


**2a** **6a**

**Figure 1.** Preferred conformations of **2a** and **6a** as determined by $^1$H NMR.

On the other hand, *J* values for azines **3** indicate an *all-anti-trans* conformation, like that found for aldehyde **7**.[18]

The electrochemical properties of new extended TTFs **2** and **3** were studied by cyclic voltammetry and relevant data are collected in Table 1. For the sake of comparison, the oxidation potentials of the azino derivatives **1** (R = Me) and the *all*-carbon analogues **8**[15] and **9**[19] are also shown.



**8** (n = 2, R = H)
**9** (n = 3, R = Me)

In positive direction, the electrochemical behaviour of compounds **2** and **3** exhibits a two-electron quasi reversible process at 10 V/s. At low scan rate (0.1 V/s), the process becomes irreversible, pointing to an EEC mechanism (Fig. 2).

**Table 1.** Oxidation potentials of donors[a]

| Compound | **1** (R: Me) | **2a** | **2b** | **3a** | **3b** | **8** | **9** |
|---|---|---|---|---|---|---|---|
| $E_{pa}$ | 0.87[b] | 0.69 | 0.63 | 0.59 | 0.56 | 0.18[c] | 0.14[d] |

[a] *E* in *V* versus SCE, Pt working electrode, $TBAPF_6$ 0.4 M in MeCN, scan rate 10 V/s.
[b] From Ref. 6 (in $CH_2Cl_2$, scan rate 0.1 V/s).
[c] Recalculated from Ref. 15 (in MeCN, scan rate 0.043 V/s).
[d] $E_1^{1/2}$ value recalculated from Ref. 19 (in MeCN, scan rate 0.1 V/s).

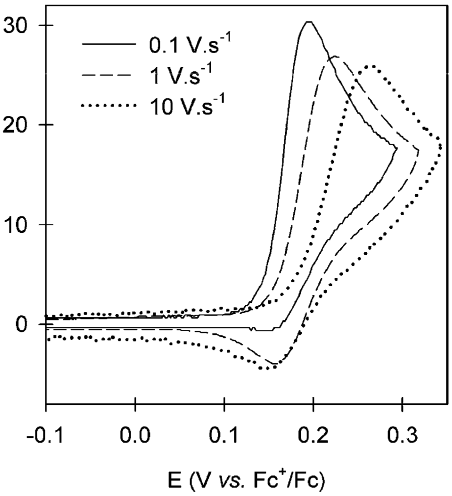


**Figure 2.** Normalized cyclic voltammograms of **2b** at different scan rates.

It is noteworthy that this behaviour is completely different to that of the shorter derivative **1** (R = Me), which displays two reversible monoelectronic oxidation waves.[6]

As expected, the replacement of hydrogen atoms by methyl groups (cf. series **a** and **b**) and the lengthening of the π-spacer (cf. **1** (R = Me), **2** and **3**) give rise to a decrease in the oxidation potentials. Moreover, the replacement of CH groups of the spacer by nitrogen atoms results in higher oxidation potentials (cf. **2a** and **8**, and **3b** and **9**), in agreement with previous reports.[24] Nevertheless, compounds **2** and **3**, like **8** and **9**, are oxidized directly to their corresponding dications, which indicates that the introduction of an azino spacer in **2** and **3** does not increase the stability of the cation radical species to a noticeable extent, in sharp contrast to the behaviour observed in related diselenadiazafulvalenes.[25]

To sum up, the newly prepared *N*-(diethoxyphosphinyl)-hydrazones **5** allow an easy access to long, unsymmetrical aza-analogues of extended TTFs **2** and **3**. Azines **2** show an *s-cis* conformation whereas compounds **3** display an *all-anti-trans* geometry. Unlike azine **1** (R = Me), which is oxidized stepwise to its cation radical and dication states, compounds **2** and **3** are directly oxidized to the corresponding dications.

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14. Analytical data. For **5a**: mp: 72 °C; IR (Nujol): 3093, 1568, 1231 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta$ (ppm) 1.31 (t, $J = 8$ Hz, 6H), 4.06–4.20 (m, 4H), 5.80 (d, $J_{H-P} = 19$ Hz, 1H), 6.41 (d, $J = 7.5$ Hz, 1H), 6.46 (d, $J = 7.5$ Hz, 1H); HRMS (EI) calcd for $C_7H_{13}N_2O_3PS_2$ (found): 268.0105 (268.0090). For **5b**: mp: 122 °C; IR (Nujol): 3106, 1566, 1242 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta$ (ppm) 1.33 (t, $J = 7.3$ Hz, 6H), 1.99 (s, 3H), 2.01 (s, 3H), 4.14 (m, 4H), 5.29 (d, $J_{H-P} = 19$ Hz, 1H). HRMS (EI) calcd for $C_9H_{17}N_2O_3PS_2$ (found): 296.0418 (296.0406).
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16. Analytical data. For **2a**: mp: 128 °C; IR (Nujol): 1502, 1536 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta$ (ppm) 6.39 (dd, $J = 5.6$ Hz, $J' = 1.5$ Hz, 1H), 6.56 (d, $J = 6.8$ Hz, 1H), 6.63 (d, $J = 2.0$ Hz, 1H), 6.66 (d, $J = 2.0$ Hz, 1H), 6.75 (dd, $J = 6.8$ Hz, $J' = 1.5$ Hz, 1H), 8.11 (d, $J = 5.6$ Hz, 1H); HRMS (EI) calcd for $C_8H_6N_2S_4$ (found): 257.9414 (257.9429). For **2b**: mp: 138 °C; IR (Nujol): 1567 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta$ (ppm) 2.06 (s, 3H), 2.11 (s, 3H), 6.22 (d, $J = 5.7$ Hz, 1H), 6.46 (d, $J = 7.1$ Hz, 1H), 6.72 (d, $J = 7.1$ Hz, 1H), 8.07 (d, $J = 5.7$ Hz, 1H); HRMS (EI) calcd for $C_{10}H_{10}N_2S_4$ (found): 285.9727 (285.9722).
17. Analytical data. For **3a**: mp: 154 °C; IR (Nujol): 1501, 1585 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta$ (ppm) 1.93 (s, 3H); 1.95 (s, 3H), 6.14 (d, $J = 11.2$ Hz, 1H), 6.18 (dd, $J = 14.5$ Hz, $J' = 9.6$ Hz, 1H), 6.46–6.59 (m, 3H), 7.96 (d, $J = 9.6$ Hz, 1H); HRMS (EI) calcd for $C_{12}H_{12}N_2S_4$ (found): 311.9883 (311.9876). For **3b**: IR (Nujol): 1580 cm$^{-1}$; $^{1}$H NMR (CDCl$_3$): $\delta$ (ppm) 1.92 (s, 3H), 1.95 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 6.13 (d, $J = 11.4$ Hz, 1H), 6.17 (dd, $J = 14.7$ Hz, $J' = 9.9$ Hz, 1H), 6.47 (dd, $J = 14.7$ Hz, $J' = 11.4$ Hz, 1H), 7.93 (d, $J = 9.9$ Hz, 1H); HRMS (EI) calcd for $C_{14}H_{16}N_2S_4$ (found): 340.0196 (340.0186).
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23. Compound **6a**: $^1$H NMR ($CDCl_3$): $\delta$ (ppm) 6.78 (dd, $J = 1.9$ Hz, $J' = 1.5$ Hz, 1H), 6.81 (d, $J = 6.5$ Hz, 1H), 6.87 (dd, $J = 6.5$ Hz, $J' = 1.5$ Hz, 1H), 9.34 (d, $J = 1.9$ Hz, 1H).
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