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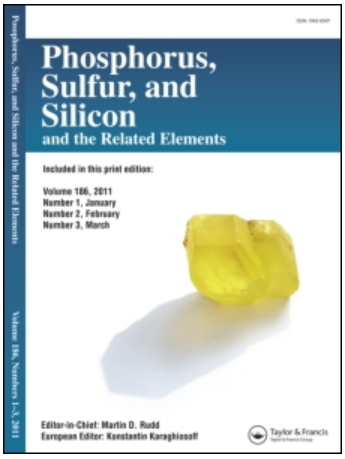

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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Aza-Analogues of Extended Tetrathiafulvalenes

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To cite this Article Andreu, R. , Garín, J. , López, C. , Orduna, J. and Levillain, E.(2005) 'Aza-Analogues of Extended Tetrathiafulvalenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1471 — 1472
To link to this Article: DOI: 10.1080/10426500590913177
URL: http://dx.doi.org/10.1080/10426500590913177

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Phosphorus, Sulfur, and Silicon, 180:1471–1472, 2005
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500590913177

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Aza-Analogues of Extended Tetrathiafulvalenes

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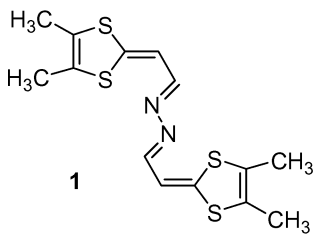
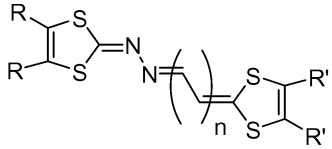
Highly extended sulfur-rich tetrathiafulvalene derivatives are known to lead to original two-dimensional associations with noticeable electrochemical features. Different conjugated spacers have been introduced to separate two (or more) 1,3-dithiole units, polyenic chains being the most used. In this context, a literature search revealed only two examples of 1,3-dithiole derivatives containing azine spacers.[1]

In this context, we have prepared compounds **1** and **2a–d** (Figure 1), by reaction of 1,3-dithiole-derived aldehydes or 1,3-dithiolium salts with hitherto undescribed 1,3-dithiole(diethoxyphosphinyl)hydrazones.



1



2a-d

a: R, R' = H; n = 1
b: R = H; R' = CH_3; n = 1
c: R = H; R' = CH_3; n = 2
d: R, R' = CH_3; n = 2

FIGURE 1

Received July 9, 2004; accepted October 5, 2004.

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TABLE I Oxidation Potentials of Donors

Compound	**2a**	**2b**	**2c**	**2d**
Ep_a (V)	0.265	0.205	0.165	0.140

Compounds **2a–d** exhibit under standard conditions (100 mVs^{-1}) one irreversible oxidation involving a two-electron transfer. With increasing scanning rate, oxidation becomes more reversible and potentials are shifted to more positive values. Both features indicate an EEC mechanism. The redox potentials of **2a–d** obtained at 10 Vs^{-1} (*vs.* Fc^+/Fc, Pt working millielectrode, 0.4 M $TBAPF_6$ in CH_3CN) are collected in Table I.

We observe that the incorporation of methyl groups on the dithiole unit and the increase of the conjugated spacer length give rise to a decrease in Ep_a values.

By comparing compounds **2a** and **2c** with their C—C analogues,[2] we can conclude that the insertion of an azino spacer (i) makes the oxidation of 1,3-dithiole units irreversible and (ii) shifts the potentials toward more positive values. This accounts for poor conjugation along the azine bridge.

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