A New Route to Dithiadiazafulvalene Derivatives from Mesoionic Thiazoles. Formation of a Ten-membered Macrocycle by Oxidation with Oxygen and in situ Generation of a Charge Transfer Complex with Tetracyanoquinodimethane

Mohammed Bssaibis,[a] Albert Robert,*[a] Pierre Lemaguerès,[b] Lahcène Ouahab,[b] Roger Carlier[c] and André Tallec[c]

[a] Laboratoire de Chimie Structurale, URA CNRS 704, Campus de Beaulieu, 35042 Rennes Cédex, France
[b] Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS 1495, Campus de Beaulieu, 35042 Rennes Cédex, France
[c] Laboratoire d'Electrochimie, URA CNRS 439, Campus de Beaulieu, 35042 Rennes Cédex, France

Mesoionic thiazoles are starting materials for the preparation of oxygen sensitive dithiadiazafulvalenes, which can be reacted in situ with acceptor derivatives to give the corresponding charge transfer complexes while their reaction with oxygen leads to a ten-membered macrocycle.

The first dithiadiazafulvalene (DTDAF), the aza analogue of tetrathiafulvalene (TTF), was reported in 1964 by Metzger et al.[1] A few alkyl substituted DTDAF derivatives were recently detected electrochemically but these derivatives are air sensitive and oxidation occurred during isolation.[2,3] The coupling of a selone with P(OMe)$_3$ enabled Tormos et al. to prepare the first uncondensed crystalline DTDAF bearing two withdrawing ester groups directly linked to the DTDAF core.[4]

In this paper we report a new synthesis of air sensitive DTDAF 5 allowing in situ generation of a charge transfer complex 7 between DTDAF and tetracyanoquinodimethane (TCNQ). We also show that DTDAF is oxidised by oxygen to a stable ten-membered macrocyclic ring 6.

As we have previously reported, mesoionic dithioles 1 are valuable starting materials for the preparation of TTF derivatives,[5] we have carried out by analogy the conversion of mesoionic thiazoles 2[6] into DTDAF derivatives 5 (Scheme 1).

According to Scheme 1 the DTADF derivatives 5 are

obtained by the addition of NEt$_3$ to a MeCN solution of 4 under argon at room temperature. Under these conditions 5 is stable and can be characterized by ^{1}H NMR and cyclic voltammetry. However 5 is very air sensitive. For instance, we observe in the mass spectra of 5 (R^1 = p-ClC$_6$H$_4$, R^2 = Me, Ar = Ph; M calc. = 634.01993, M$^{\cdot+}$ found = 634.0160) the presence of the oxidation product 6 (1/2 M calc. = 333.0049, M$^{\cdot+}$ found = 333.006). The voltammogram of 5 (R^1 = p-ClC$_6$H$_4$, R^2 = Me, Ar = p-NO$_2$C$_6$H$_4$) is given as an example (Fig. 1).

It appears that DTDAF derivatives are very good donors showing two 'quasi-reversible' peaks of equal intensity. The first and second oxidation potentials are similar to the corresponding values reported for other DTDAF derivatives.[2,4] It is worth noting that during the second scan the first oxidation peak is shifted from −0.03 to −0.04 V vs. saturated calomel electrode. Moreover the voltammogram remains unchanged during further scans. This interesting feature has
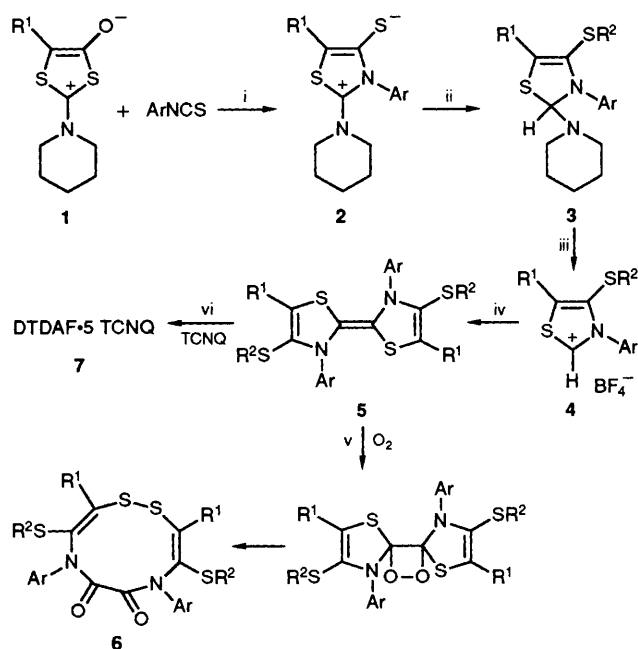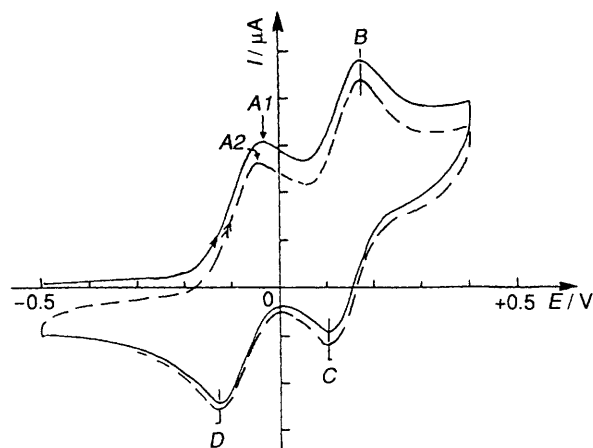
Scheme 1 Synthesis of DTDAF derivatives 5 and their oxidation products 6 or their charge transfer complexes 7. *Reagents and conditions*: i, boiling C_6H_6, 2 h, 80% yield; ii, R^2X CH_2Cl_2, room temp. 10 h, then 5 equiv. piperidine and 2 equiv. $NaBH_4$, 10 min, room temp., 60% yield; iii; CH_2Cl_2, HBF_4–diethyl ether, 0 °C, 2 h, 80% yield; iv, MeCN under argon, then NEt_3, room temp., 30 min 65% yield; v, heating 5 for 5 min in EtOH–C_6H_6, 60% yield of 6; vi, during the preparation of 5 5 equiv. TCNQ is added, 70% yield of 7

Fig. 1 Cyclic voltammogram of 5: NBu_4PF_6 0.5 mol dm^{-3} MeCN; platinum electrode 1 mm²; scanning rate: 0.1 V s^{-1}; *vs.* saturated calomel electrode. *A1*: $E = -0.03$ V; *A2*: $E = -0.04$ V; *B*: $E = +0.17$ V; *C*: $E = +0.10$ V; *D*: $E = 0.13$ V.

Fig. 2 ORTEP drawing of 6 ($R^1 = p$-MeC$_6$H$_4$, R^2 = Me, Ar = Ph)

already been observed with TTF analogues and it was demonstrated that the neutral TTF adopted a *trans* configuration in the solid state while for a corresponding radical cation salt the TTF·⁺ adopted a *cis* configuration.[7] We therefore suggest that the shift between the first and second scan for the first oxidation peak is the result of a *trans* → *cis* isomerisation of DTDAF 5 at the DTDAF·⁺ stage.
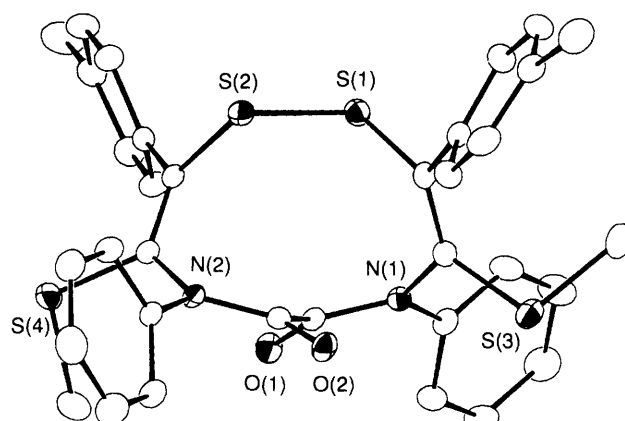
The DTDAF derivatives 5 are easily oxidized and converted into the macrocycle 6 by a simple recrystallization in EtOH in the presence of air. The structure of such a ten-membered macrocycle including a sulfur–sulfur linkage is established by IR and ¹H NMR spectroscopy as well as by an X-ray diffraction study (Fig. 2).†

It is worth noting that a similar ten-membered macrocycle was very recently obtained by oxidation of a bisthiazolium salt but only by using superoxide.[8]

The synthetic strategy used to prepare 5 allows the addition of an acceptor derivative in the medium during the synthesis. It is then possible to isolate a stable charge transfer complex. When TCNQ is added during the preparation of 5 ($R^1 = p$-ClPh, R^2 = Me, Ar = Ph), 7 is obtained as a dark powder (m.p. 230 °C) characterized in FTIR (KBr diffuse reflectance spectra) by a very broad band (4400–1600 cm^{-1}) and another broad band at 1372 cm^{-1}. On the other hand the v_{CN} of TCNQ shifted from 2227 to 2194 cm^{-1} suggesting a partial charge transfer from DTDAF to TCNQ[9] consistent with these results a single crystal conductivity of 6 × 10^{-4} Ω^{-1} cm^{-1} was observed for 7. The crystal structures and physical characteris-

tics of these TCNQ (stoichiometry 1 DTDAF: 5 TCNQ) salts are currently under examination.‡

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