



# Fulvalene derivatives: strong proaromatic electron acceptors

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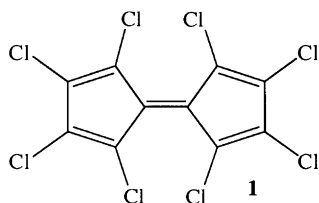
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**Abstract**—Synthesis and electrochemical properties of novel proaromatic electron acceptors based on the fulvalene parent system are described. © 2001 Elsevier Science Ltd. All rights reserved.

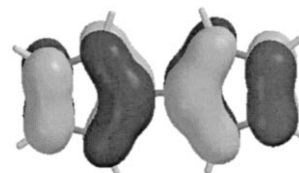
Whereas a variety of strong electron donors have been involved in the study of conducting charge-transfer complexes during the past decades, the choice of electron-accepting components is limited mostly by *p*-quinoid derivatives.<sup>1,2</sup> Evidently, the best organic conductors consist of a donor that generates a new aromatic sextet upon oxidation and an acceptor that undergoes the same conversion upon a one-electron reduction.<sup>3</sup> The proaromaticity of *p*-quinoid acceptors is a key feature that leads to the enhanced stability of the corresponding reduced forms and, as a consequence, plays a significant role in the design of new electroactive components. Formally, the fulvalene framework corresponds to the proaromaticity requirement, it constitutes a fragment of the electron-accepting C<sub>60</sub> molecule,<sup>4</sup> and has been known for years.<sup>5</sup> However, fulvalenes have received only scant attention as  $\pi$ -electron acceptors, probably due to the instability of the parent compound. Although almost 30 years ago the formation of charge-transfer complexes between octachlorofulvalene (**1**) and a variety of aromatic donors were observed,<sup>6</sup> a quantitative study of the electron-accepting ability of compound **1** and the stability of the corresponding anion radical and dianion have never been studied.



The fulvalene molecule belongs to the same  $d_{2h}$  symmetry group as tetrathiafulvalene TTF and its  $\pi$ -type delocalised LUMO is of the of the same  $b_{2g}$  symmetry as that of tetracyanoquinodimethane TCNQ (Fig. 1). Derivatives of fulvalene are, therefore, highly attracting potential components for charge-transfer complexes. Semiempirical NDO calculations using AM1 parameterisation (Hyperchem, version 5.0) predict a sharp increase in accepting ability upon attachment of accepting substituents to the fulvalene moiety. Thus, the LUMO energy for fulvalene itself is  $-1.38$  eV, whereas it is  $-2.12$  eV for 2,3,6,7-tetrachlorofulvalene (planar equilibrium geometry predicted),  $-2.17$  eV for 1,4,5,8-tetrachlorofulvalene (non-planar), and  $-2.71$  eV for octachlorofulvalene (non-planar). For comparison, the calculated LUMO energy for TCNQ is  $-2.92$  eV.

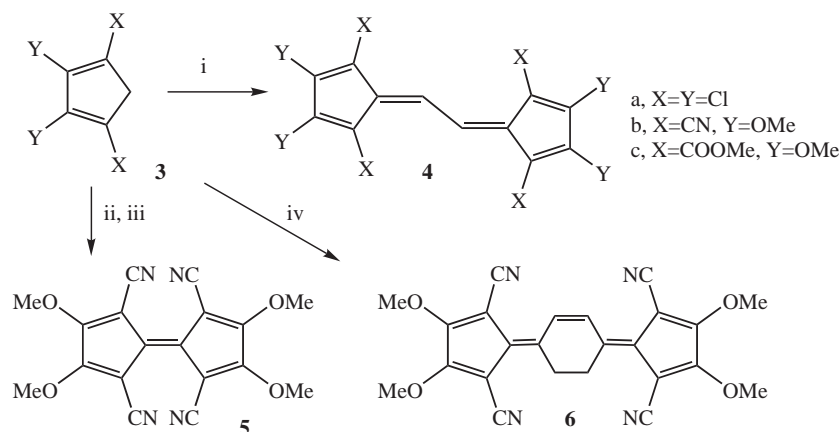
In fact, the only fulvalene studied by the CV technique is 2,3,6,7-tetraamino-1,4,5,8-tetracyanofulvalene derivative **2**, involving both powerful accepting and donating substituents.<sup>7</sup> In spite of the presence of four amino groups, **2** exhibited a two-electron reversible reduction step.<sup>8</sup> Replacing the amino functions by less donating substituents should increase the electron-accepting strength.

In this communication, we report the electrochemical properties of octachlorofulvalene (**1**) and the synthesis



**Figure 1.** LUMO of fulvalene.

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**Scheme 1.** Reactions and conditions: (i) glyoxal bis(dimethylacetal), AcOH/piperidine,  $\Delta$ ; (ii) *t*-BuOK/THF; (iii) AgNO<sub>3</sub>; (iv) 1,4-cyclohexanedione, DMF/piperidine, rt, 2 h.

and electrochemical properties of novel fulvalene derivatives **4–6**. Octachlorofulvalene was prepared according to the reported procedure.<sup>9</sup> The synthesis of its vinylog **4a** was achieved by condensation of tetrachlorocyclopentadiene **3a** with glyoxal bis(dimethylacetal)<sup>†</sup> (Scheme 1). The cyclic voltammetry (CV) of **1** exhibits two reversible one-electron reduction peaks at 0.213 and –0.256 V (Table 1), corresponding to the successive reduction to the anion radical and dianion, respectively.

Judging by the first reduction potential, fulvalene **1** possesses strong electron-accepting properties comparable to that of TCNQ (0.269 V under the same experimental conditions). Moreover, the difference between the two reduction peaks of **1** (0.469 V) is smaller than that of TCNQ (0.559 V), indicating the enhanced stability of the dianion derived from **1**. The CV of vinylog **4a** exhibits two reversible one-electron reduction peaks (Table 1). As expected, the increased conjugated link between the two fulvene moieties brings about a considerable decrease in the electron-accepting ability and in the difference between the two reduction potentials. This behaviour is attributed to the enriched  $\pi$ -electron character and lower coulombic repulsion due to the enhanced size of the molecule. A similar negative shift in the redox potentials and a decrease in the difference between redox potentials were observed for the vinylogs of TTF<sup>10</sup> and BEDT–TTF<sup>11</sup> with respect to the parent donors. It is noteworthy that, in the presence of oxygen and at low reduction rate, both the generated anion radical and the dianion of **1** appeared to be unstable and elimination of the chloride anion occurred.

The stability of the ionic species can be increased when the halogen atoms are replaced by functional groups. Thus, fulvalene **5** and its vinylog **4b** were synthesised starting from 1,4-dicyano-2,3-dimethoxycyclopentadiene **3b**, as outlined in Scheme 1. Unexpectedly, derivative **6** formed in a high yield when 1,4-cyclohex-

anedione was used. By applying the same experimental procedure, vinylog **4c** was prepared from the corresponding 1,4-dimethoxycarbonyl-2,3-dimethoxycyclopentadiene **3c**. Fulvalene **5** is non-planar (Fig. 2) and the dihedral angle between the two cyclopentadiene moieties is 26.9°.<sup>‡</sup>

Similar to octachlorofulvalene, fulvalene **5** exhibits two one-electron reduction steps. However, the difference between the two reduction potentials does not exceed 0.086 V and the first reduction step occurs at –0.24 V, about 0.3 V more positive than C<sub>60</sub>, indicating moderate electron-accepting ability. Interestingly, the calculated LUMO energy of **5** is –2.25 eV, demonstrating good correlation between the experimental redox potentials and AM1 predictions for this class of compounds. Insertion of additional double bonds, as in derivatives **4b** and **6**, leads to a further decrease in the electron-accepting ability and to the coalescence of the two one-electron reduction steps into one two-electron step, indicating a diminished coulombic repulsion with

**Table 1.** Electrochemical data (in CH<sub>2</sub>Cl<sub>2</sub>, *n*-Bu<sub>4</sub>PF<sub>6</sub> (0.1 M); 400 mV s<sup>–1</sup>; versus Ag/AgCl)

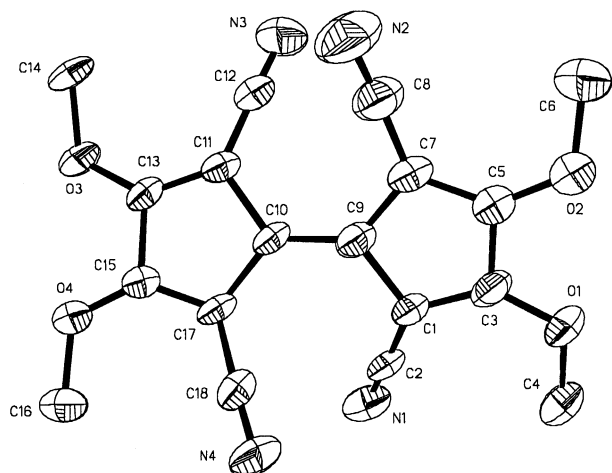
Compound	$E^1_{\text{red}}$ (V)	$E^2_{\text{red}}$ (V)	$\Delta E_{1/2}$ (V)
<b>1</b>	0.231	–0.256	0.469
<b>4a</b>	–0.320	–0.494	0.174
<b>4b</b>	–0.468 <sup>a</sup>		
<b>4c</b>	–0.410 <sup>a,b</sup>		
<b>5</b>	–0.240	–0.326	0.086
<b>6</b>	–0.375 <sup>a</sup>		
TCNQ	0.269	–0.330	0.599

<sup>a</sup> Two-electron process.

<sup>b</sup> Irreversible.

<sup>‡</sup> A red plate of **5** (0.08×0.3×0.4 mm) is triclinic: C<sub>18</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>, space group  $P\bar{1}$ ,  $Z=2$ , at 293(2) K,  $a=9.301(3)$ ,  $b=10.147(4)$ ,  $c=10.197(4)$  Å,  $\alpha=112.098(7)$ ,  $\beta=99.951(8)$ ,  $\gamma=95.139(9)^\circ$ .  $V=865.5(5)$  Å<sup>3</sup>,  $\rho_{\text{calcd}}=1.337$  Mg m<sup>–3</sup>,  $F(000)=360$ . Atomic coordinates, bond lengths and angles and anisotropic parameters have been deposited at the Cambridge Crystallographic Data Centre, deposition number 154009.

<sup>†</sup> All new compounds were characterised by <sup>1</sup>H NMR and HRMS. The structures of **3b**, **3c**, **4c** and **6** have also been confirmed by X-ray diffraction experiments.



**Figure 2.** Molecular structure of **5**. Selected bond lengths: 1.367(5) Å (C1–C3), 1.472(5) Å (C1–C9), 1.452(6) Å (C3–C5), 1.368(5) Å (C9–C10), 1.326(5) Å (C3–O1).

a better stabilisation of the corresponding dianion. The electron-accepting properties of vinylog **4c** resemble that of the other analogues; however, the two-electron reduction step observed for this derivative is not reversible.

In accordance with the present study, octachlorofulvalene is the strongest  $\pi$ -electron acceptor known today within the fulvalene family. Mixing of stoichiometric amounts of this acceptor with TTF in benzonitrile leads to oxidation of the latter, evidenced by the appearance of absorption bands at 446 and 585 nm, characteristic for the TTF cation radical. Formation of a charge-transfer complex, characterised by the appearance of a weak charge-transfer band centred at 1020 nm, was observed with BEDT–TTF under the same conditions. Fulvalene **1** forms an ion radical salt with TTF also in the solid state; the conductivity of this salt measured on compressed pellets was around 1 S cm<sup>−1</sup>. Efforts to

know precisely the structural features of ion radical salts and complexes involving **1** as the accepting component are underway.

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