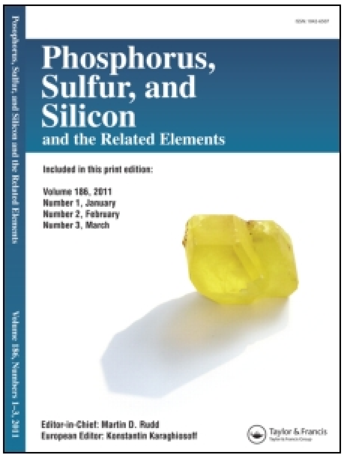

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Synthesis and Properties of a BenzoquinoneDihydrotetrathiafulvalene Diad

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Synthesis and Properties of a Benzoquinone-Dihydrotetrathiafulvalene Diad

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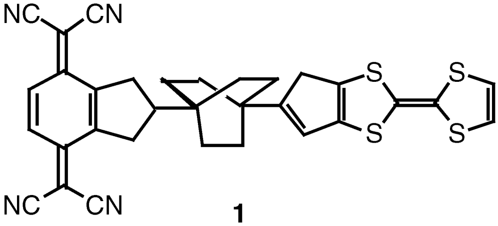
*A new donor–acceptor diad compound **6** with the donor dihydro-TTF and acceptor quinone functions in very close proximity has been prepared and characterized. The X-ray structure shows an interesting stacking pattern and electrochemically it undergoes two reversible oxidations and two reversible reductions. An ESR signal has been observed due to thermal population of the radical anion/radical cation state.*

Keywords Donor–acceptor; quinone; tetrathiafulvalene

Ever since Aviram and Ratner suggested a theoretical "molecular rectifier" **1** consisiting of a TTF donor and TCNQ acceptor connected by an insulating linker,[1] there has been considerable interest in preparing and studying the properties of such systems,[2] and such components will be required for the rapidly developing field of molecular electronics.[3]



1

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We thank A. M. Z. Slawin (St. Andrews) for determining the X-ray structure, J. A. Crayston (St. Andrews) for assistance with the cyclic voltammetry measurements, and J. C. Walton (St. Andrews) for making the ESR measurements.

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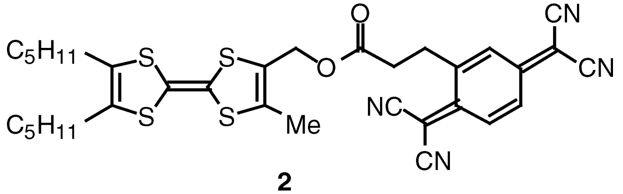
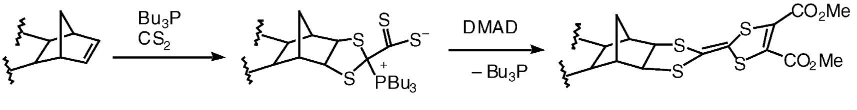
At the end of 2003, Bryce and coworkers reported the TTF-TCNQ diad **2** with a remarkably low HOMO-LUMO gap (0.17V), which gave an ESR signal due to the thermally populated diradical.[4]



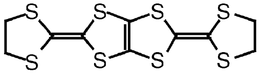
2

We now present our version of the donor–acceptor (D–A) compound design. The synthesis of the compound shown in Scheme 1 relies on our method of directly functionalizing strained double bonds to give a dihydro-TTF using $Bu_3P{\cdot}CS_2$ and DMAD.[5]



SCHEME 1

Although these products have a dihydro-TTF rather than the fully unsaturated structure, they may still show useful electrical properties since many of the donors recently developed by the group of Yamada such as **3**,[6] **4**,[7] and **5**[8] also contain a dihydro-TTF.



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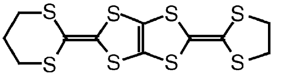

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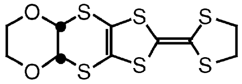

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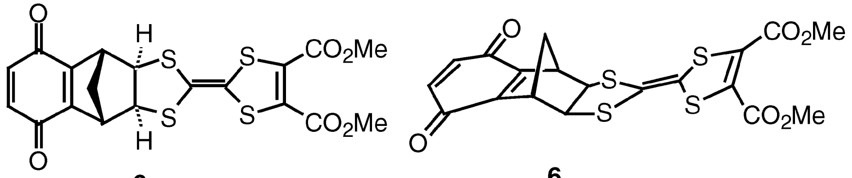
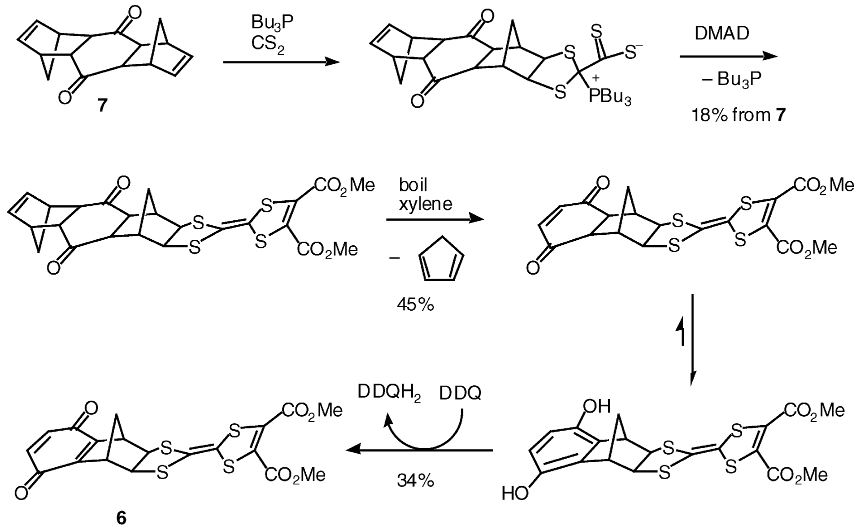
The chosen target compound **6** is shown in Scheme 2 in two representations. It has perhaps the most direct and rigid link between the donor and acceptor functions in a D–A compound so far.



6 **6**

SCHEME 2

Our synthetic approach started from the bis-cyclopentadiene Diels–Alder adduct of benzoquinone **7** which reacts in the dihydro-TTF forming reaction on one side only. In this way the other cyclopentadiene



serves to protect the quinone double bond against Michael addition of Bu_3P and other unwanted side reactions. Once it has performed this function it is removed in a retro Diels–Alder reaction.

The resulting 2,3-dihydroquinone structure exists almost entirely as the more stable aromatic hydroquinone form and this allows its oxidation to the target compound **6** using DDQ. Although the overall yield is only about 3%, the sequence is short and all starting materials are readily available, so the compound has been obtained in sufficient quantity for detailed characterization.

The compound exists as shiny black needles, mp 168–170°C, which gave correct elemental analysis and spectroscopic data. The structure was readily confirmed by a single crystal X-ray diffraction study which gave the structure shown in Figure 1.

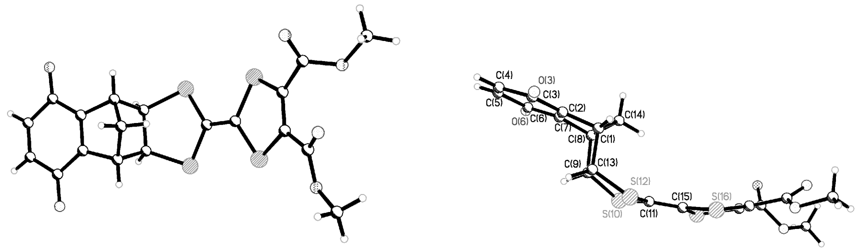


FIGURE 1 Molecular structure of compound **6** as viewed from above and from the side.

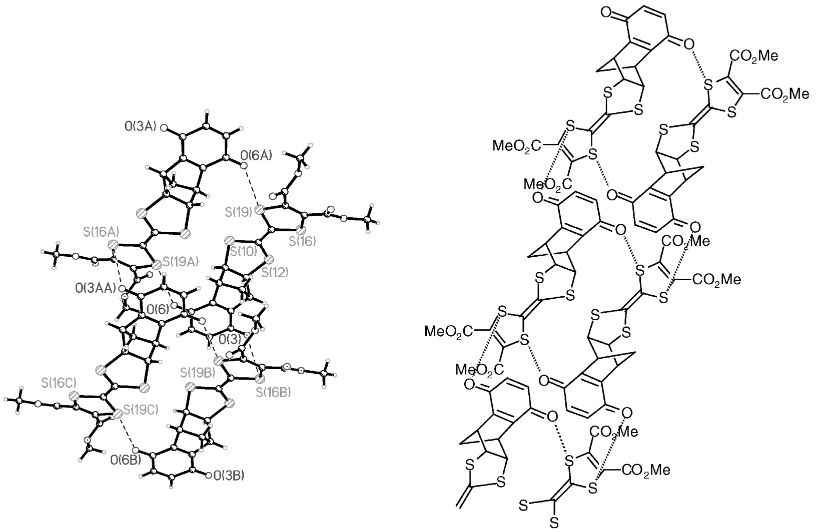


FIGURE 2 Stacking pattern for compound **6** from X-ray diffraction.

This shows that the dihydro-TTF and quinone systems are almost parallel with the rigid spacer, ruling out any intramolecular through-space interaction. The stacking pattern in the solid state shows significant intermolecular interactions with head-to-tail pairs of molecules stacked up in a long ribbon arrangement (Figure 2).

Under cyclic voltammetry conditions the compound shows two reversible oxidations at +0.5 V and +0.9 V (relative to ferrocene/Fc$^+$) and two reversible reductions at −0.8 V and −1.4 V. However, there is also a third irreversible reduction wave (approximately −2.0 V), probably corresponding to undesired reaction of the ester groups. The difference of 1.3 V between the first oxidation and reduction potentials is obviously far larger than for compound **2**, where it was only 0.17 V. However, we still felt it would be worthwhile attempting to observe an ESR signal for **6**. The result is shown in Figure 3 below. The obvious signal is accompanied by a slight shoulder to the right exactly as in the spectrum of **2**.[4] However, whereas Bryce and coworkers estimated about 0.7% of compound **2** to be in the diradical state at 290 K, compound **6** exists to an extent of only 0.03% as the diradical at the significantly higher temperature of 342 K.

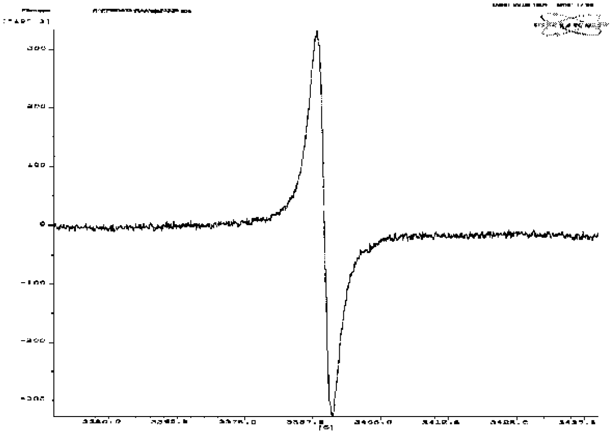


FIGURE 3 ESR spectrum recorded for compound **6** in acetonitrile.

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