A New Type of π-Electron Donors with One Dithiole Unit: Substituted 7-(1,3-Dithiol-2-ylidene)-7-hydrobenz[*d*,*e*]anthracenes

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New electron donors **11a–c** bearing only one 1,3-dithiole ring conjugated with an acene backbone have been synthesized by Wittig–Horner reactions from 7*H*-benz[*d*,*e*]anthracen-7-one (**10**) and differently substituted phosphonate esters **9a–c**. The donor properties of **11** have been characterized by means of both experimental techniques and quantum chemical calculations. Cyclic voltammetry measurements on the novel compounds predict donor abilities comparable to those of TTF and BEDT-TTF. The voltammograms show a multi-stage redox behaviour with oxidation up to the trication, where the first two oxidation processes take place at very close potentials. These processes have been assigned to a simultaneous oxidation of the dithiole and acene moieties on the basis of DFT/B3-P86/6-31G* theoretical calculations. Whereas the neutral compound and the monocation exhibit butterfly-shaped non-planar structures, the dication is fully aromatic and consists of a closed-shell, singly charged, planar polyacenic unit and a singly charged dithiole ring. The third redox process can be assigned to a second oxidation of the acene unit. The high aromaticity of the dication, coupled with the particular donor ability of the acene unit are shown to be the key factors in accounting for the electrochemical behaviour and the enhanced donor properties of the novel compounds. Theoretical calculations also help to rationalize the UV/Vis data in that they predict the appearance of a low-energy, intramolecular charge-transfer absorption band for the neutral compounds. Stable charge-transfer complexes with a 2:3 (D/A) stoichiometry have been prepared by reaction with the strong acceptors $TCNQF_4$ and DDQ.

Introduction

During the last few years, much attention has been devoted to the preparation of novel substituted π-electron donors of tetrathiafulvalene (TTF) and, particularly, to the synthesis of oligomeric and dendrimeric molecules[1] bearing two or more TTF units.[2] Simultaneously, a considerable synthetic effort has also been focused on the preparation of novel donors in which the 1,3-dithiole rings forming the parent TTF are separated by conjugated spacers. These compounds show good donor abilities and a wide variety of electrically conducting or semiconducting compounds have been reported.[3]

In contrast to the large number of π-electron donors containing two or more 1,3-dithiole rings, only a few molecules bearing just one 1,3-dithiole unit have been reported, despite the appealing donor properties they can exhibit. For instance, 2-(thiopyran-4′-ylidene)-1,3-dithioles **1**, fused with thiophene units, are found to be comparably strong electron donors as TTF.[4] Although the neutral form of **1** possesses a non-planar geometry, the radical cation is planar. 4-(1,3-Dithiol-2-ylidene)-4*H*-cyclopentadithiophenes **2** and 4-(1,3-dithiol-2-ylidene)-7*H*-cyclopentadithiophenes **3** exhibit low oxidation potentials and X-ray structural analyses show that both molecules adopt planar structures with short *intermolecular* S···S contacts.[5] Electrochemical oxidation of **2** and **3** affords the respective polymers, which after doping exhibit high electrical conductivities.

Recently, dithiapentafulvenylthiophenes **4** have been prepared in order to carry out further chemical and electrochemical oxidative coupling, leading to novel extensively π-conjugated tetrathiafulvalene analogues.[6a] This oxidative dimerization of dithiafulvalenes seems to be very general and various extended TTFs have been prepared by this procedure.[6] The oxidation potential measured for **4** is indicative of a moderate electron-donating ability (E_{ap} = 0.6−0.8 V).

On the other hand, arenes are known to show a wide variety of ionization potentials and linearly annelated polyacenes such as tetracene or pentacene are readily oxidized.[1b] *peri*-Condensed arenes are less potent donors, but form stable radical cations. In fact, perylene **5** is capable of forming electrically conducting non-stoichiometric salts.[7]

We have recently reported the preparation and redox properties of some extensively π-extended *p*-quinodimethane analogues of TTF such as **6** and **7**,[8] as well as of related dimeric compounds.[9] These compounds exhibit a first oxidation wave involving two electrons, leading directly to the formation of the dication due to the high instability of the corresponding radical cation.[8] Since this instability is associated with the highly distorted geometries found for the radical cations, more planar geometries and hence more aromatic cations could be expected if one of the two dithiole rings present in these molecules were to be removed.

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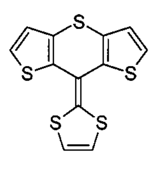

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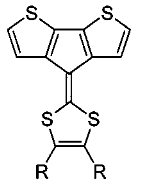

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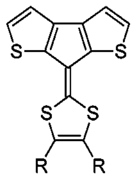

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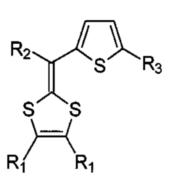

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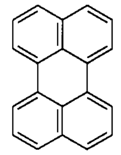

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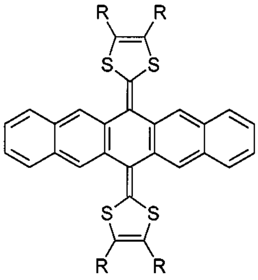

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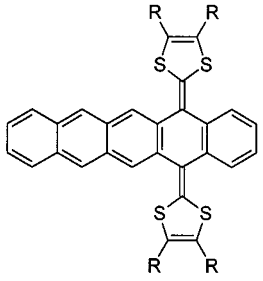

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With this in mind, we decided to combine the 1,3-dithiole ring with an arene such as benz[*d*,*e*]anthracene, thereby forming a new class of electron donors **11** with interesting electrochemical properties. Compounds **11** possess an extended π-conjugation, which decreases on-site coulombic repulsions and, in addition, the presence of sulfur atoms in the 1,3-dithiole rings might lead to *inter*molecular interactions in the stacking direction. The presence of different sulfur-containing substituents on the 1,3-dithiole ring may reinforce these *inter*molecular interactions. In this study, we combine spectroscopic and electrochemical data with theoretical calculations with the aim of achieving a better understanding of the geometrical and electronic properties of these novel donors.

Results and Discussion

Synthesis

The 1,3-dithiol-2-ylidenes **11a−c** were prepared from commercially available 7*H*-benz[*d*,*e*]anthracen-7-one **10** by Wittig−Horner reactions with the carbanions **9**, which were generated from the corresponding phosphonate esters **8a−c**[10] by treatment with *n*-butyllithium (Scheme 1). The starting phosphonate esters **8** were in turn prepared according to multi-step literature procedures.[11] Compounds **11a−c** were obtained as stable, orange, microcrystalline solids in moderate yields.[12]

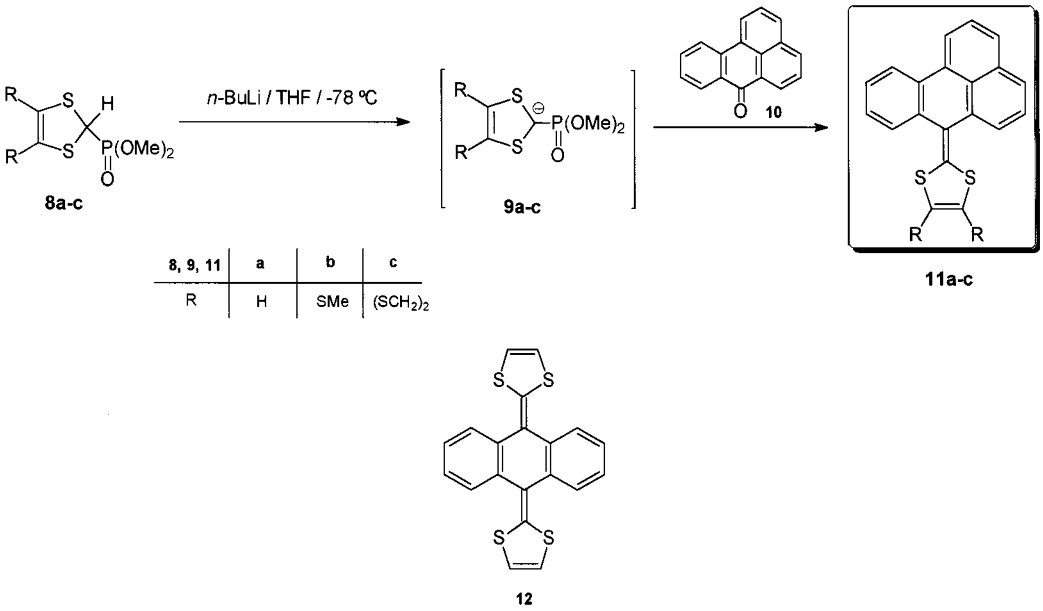
The analytical and spectroscopic data are in full agreement with the proposed structures. Interestingly, the electronic spectra of compounds **11a−c** show an absorption band at $\lambda \approx 440$ nm, similar to that previously reported for the π-extended donors **6** and **7**,[8a] which can reasonably be assigned to a photoinduced *intra*molecular charge-transfer (see theoretical calculations).

Electrochemical Properties

The electrochemical properties of compounds **11a−c** were studied by cyclic voltammetry. Measurements were made in dichloromethane solution at room temperature using a glassy carbon electrode with tetrabutylammonium perchlorate as the supporting electrolyte. The CV data are collected in Table 1, together with those for TTF and compounds **6** and **7** measured under the same experimental conditions for comparison purposes.

Compounds **11a** and **11c** show two one-electron oxidation waves, corresponding to formation of the radical cation and dication species. The first oxidation potential is shifted toward more positive values compared to that of the TTF molecule, indicating that these molecules are slightly less strong donors than TTF. The potential measured for **11a** is, however, quite similar to those found for the well-known donor BEDT-TTF ($E^1_{ox} = 0.51$ V) and other previously reported bis(TTF) derivatives.[1a,1b,13] The second oxidation potential of **11a** is similar to that of TTF. The oxidation potentials of **11c** are anodically shifted with respect to those of **11a**, as is to be expected for ethylenedithio-substituted 1,3-dithiole rings. Donor **11b** exhibits only one oxidation wave, involving two electrons, as here the first two oxidation waves, which are very close in the related analogues **11a** and **11c**, are actually coalesced.

The small differences between the first two oxidation potentials of compounds **11a** and **11c** (coalescing in the case of **11b**) (see ΔE_{ox} in Table 1) indicate that the radical cations are easily oxidized to the dications. This electrochemical behaviour is similar to that observed for compounds **6** and **7**, which give a single two-electron oxidation wave leading directly to the dication. Compounds **11** also show, like compounds **6** and **7**, the presence of a third oxidation process at around 1.4 V. On the basis of the assignment made for **6** and **7**,[8] this process can reasonably be attributed to the oxidation of the acene unit. The value of 1.4 V is indeed



Scheme 1

Table 1. Electronic spectra and cyclic voltammetry data for compounds **11a−c**

Compound	λ_{max} [nm][a]	$E^1_{a.p.}$[b]	$E^2_{a.p.}$[b]	ΔE_{ox}	$E^3_{a.p.}$[b]
11a	438	0.58	0.76	0.18	1.34
11b	438	0.75 (2 e^-)		−	1.37
11c	446	0.70	0.83	0.13	1.37
6	415	0.50 (2 e^-)		−	1.48
7	458	0.49 (2 e^-)		−	1.31
TTF	−	0.37	0.70	0.33	−

[a] In CH_2Cl_2. − [b] V vs. SCE, GCE as working electrode, $Bu_4N^+ClO_4^-$ (0.1 M) as supporting electrolyte; scan rate: 200 mV/s, CH_2Cl_2 as solvent. − [c] $\Delta E_{ox} = E^2 - E^1$.

similar to that found for the oxidation of anthracene (1.39 V) under the same experimental conditions. However, there is a big structural difference between compounds **11** and the extended TTFs **6** and **7** in that while the latter have two dithiole donor units, the former have only one. The question then arises as to how the similar electrochemical behaviour shown by these two kinds of compounds can be rationalized. In the following, we present a detailed analysis of the three oxidation processes undergone by compounds **11** on the basis of theoretical calculations.

Donors **11a−c** show a quasi-reversible electrochemical behaviour where the reduction waves for reversion to the neutral molecule from the cationic species show a striking shift to negative values. This trend has previously been observed for other π-extended TTF derivatives such as **6** and **7**[8] and can be accounted for in terms of the high stability of the dicationic species (see below).

Charge-Transfer Complexes

In spite of the strong donor ability of the novel donors **11a−c**, they do not form complexes with electron acceptors such as tetracyano-*p*-quinodimethane (TCNQ) or dicyano-*p*-quinonediimine (DCNQI). They do, however, form stable charge-transfer (CT) complexes with stronger acceptors such as tetrafluorotetracyano-*p*-quinodimethane ($TCNQF_4$) and dichlorodicyano-*p*-benzoquinone (DDQ). When donors **11** are mixed with $TCNQF_4$ or DDQ in hot CH_2Cl_2, a rapid reaction takes place and a black, microcrystalline solid precipitates, which can be collected by filtration. The complexes thus formed show characteristic CT bands in the visible region of their electronic spectra. Moreover, in the IR spectra, a shift to lower frequency values for the stretching bands of the cyano and/or carbonyl groups compared to those in the neutral molecules is seen, thus confirming the presence of the CT interaction (Table 2).

Table 2. Spectroscopic and analytical data of the novel CT complexes prepared

Complex	ν [$^{-1}$][a]	λ [nm][d]	D/A/CH_2Cl_2 stoichiometry[e]
11a·$TCNQF_4$	2194, 2175[b]	862, 842, 757	2:3:1
11c·$TCNQF_4$	2192, 2171[b]	862, 844, 753	2:3:1
11a·DDQ	2225,[b] 1629[c]	468, 418	2:3:2
11c·DDQ	2225,[b] 1625[c]	456, 426	2:3:1

[a] FT IR (KBr disc). − [b] ν_{CN}. − [c] ν_{CO}. − [d] In CH_2Cl_2. − [e] Deduced from elemental analysis.

According to elemental analyses, all complexes formed have a 2:3 (D/A) stoichiometry, with one or two associated solvent molecules (CH_2Cl_2). This result, together with the vibrational frequency values found for the cyano and carbonyl groups in the IR spectra (Table 2), rules out any possibility that the acceptor molecules might have been present as the respective dianions in the complexes [ν_{CN}($TCNQF_4^{2-}$): 2167, 2133 cm^{-1}; ν_{CN} (DDQ^{2-}): 2192, 2169 cm^{-1}],[14] [ν_{CN}($TCNQF_4^-$): 2201 cm^{-1}].[15] The room-temperature conductivities of these complexes, measured as compressed pellets using a standard two-probe technique, were found to be very low ($\sigma_{RT} < 10^{-6}$ S·cm^{-1}).

Theoretical Calculations

With the aim of gaining a deeper understanding of the electrochemical and optical properties discussed above, the molecular structure and electronic properties of the unsubstituted compound **11a**, in both the neutral and oxidized states, were assessed theoretically by performing density functional theory (DFT) B3-P86/6-31G* calculations. DFT calculations have the advantage of including electron correlation effects and have been shown to predict molecular geometries of extended TTFs in better accord with experimental X-ray structural data than standard ab initio Hartree-Fock (HF) calculations.[8a]

1. Neutral 11a

The molecular structure of **11a** was optimized assuming a C_s-planar structure and without imposing any symmetry restriction. As depicted in Figure 1a, the minimum-energy conformation corresponds to a butterfly-shaped non-planar structure, similar to that found for extended TTFs such as **6** and **7**.[8a] The planar conformation is destabilized by very short contacts between the sulfur atoms of the dithiole moiety and the hydrogen atoms in *peri* positions on the acene unit. These steric contacts are found at distances of only 2.04 Å, very much shorter than the sum of the van der Waals radii (2.91 Å).[16] To avoid these interactions, the central ring of the acene unit folds into a boat conformation and the molecule adopts a butterfly structure with the lateral benzene rings pointing upwards and the dithiole ring pointing downwards.

The conformation of **11a** depicted in Figure 1a is calculated to be 13.91 kcal/mol more stable than the fully planar structure. This energy is less than half of that found using the same methodology for the extended TTF 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**12**, 37.71 kcal/mol), i.e. the anthracene analogue of **6** and **7**, in which the presence of dithiole rings on both sides of the acene unit leads to a more hindered planar structure. The tilting of the dithiole ring with respect to the mean plane formed by atoms C9, C10, C11, and C12 (see Figure 1d for atom numbering) is 30.5°, slightly smaller than the angle obtained for **12** on the basis of B3-P86/6-31G* calculations (34.0°)[8a] or from X-ray data (33.3°).[17] The average angle formed by the lateral benzene units, i.e. by the “wings of the butterfly”, is, however, significantly larger for **11a** (157.0°) than for **12** (B3-P86/6-31G*: 142.1°; X-ray: 143.8°). The acene framework is therefore less distorted from planarity in **11a** than in the extended TTFs **6**, **7**, and **12**.

Bond lengths calculated for the minimum-energy conformation of **11a** are given in Figure 1b. The optimized distances indicate that the acene unit consists of two subunits: The benzene ring formed by atoms C-11 to C-16, which retains its aromaticity having carbon−carbon bond lengths of 1.40 ± 0.01 Å, and the naphthalene unit formed by atoms C-1 to C-10, which has bond lengths almost identical to those found in the naphthalene molecule (cf. Figures 1b and 1c). These two aromatic units are linked to each other and to the 1,3-dithiol-2-ylidene moiety by carbon−carbon bonds (C1−C11, C9−C17, and C12−C17) of essentially single-bond character (1.47 Å). From a structural viewpoint, compounds **11** should therefore be viewed as three-component systems comprising benzene, naphthalene, and 1,3-dithiol-2-ylidene subunits, rather than as substituted anthracenes. The benzene and naphthalene moieties are slightly distorted from planarity, due in part to an interaction between 2-H and 16-H, which are separated by just 1.80 Å in the planar conformation.

Figure 2 shows the atomic orbital (AO) composition of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **11a**. The HOMO is mainly localized on the 1,3-dithiol-2-ylidene unit and has an energy of −5.40 eV. This energy is intermediate between that calculated for the HOMO of the 1,3-dithiol-

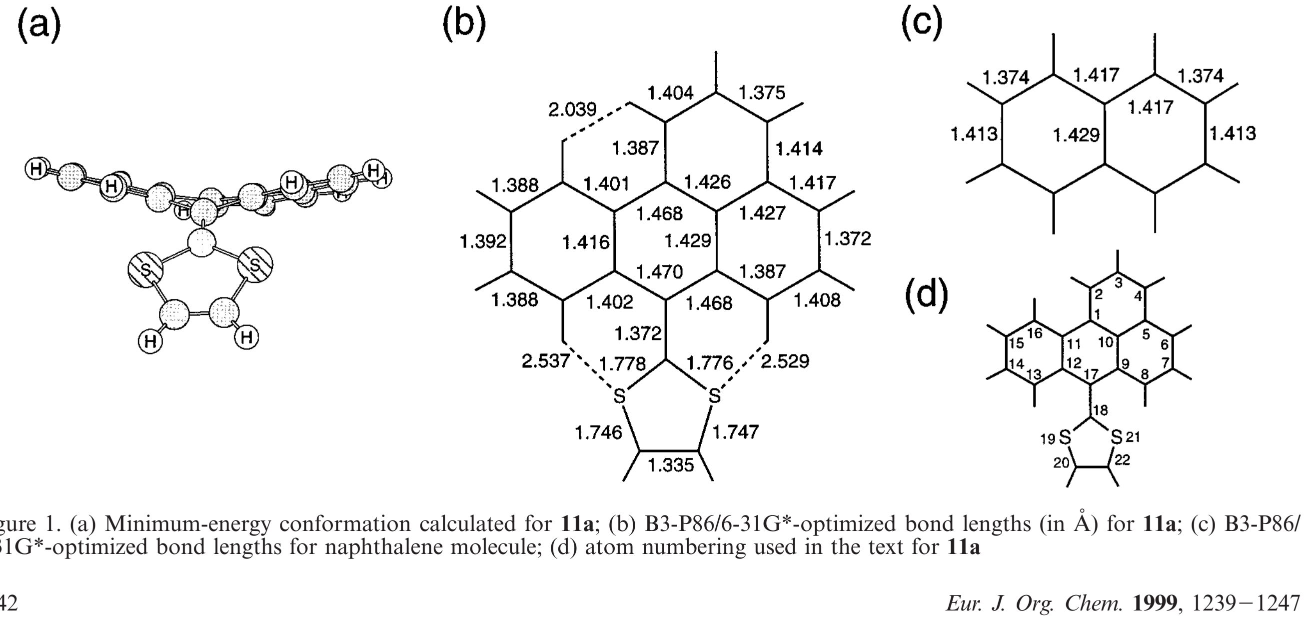


Figure 1. (a) Minimum-energy conformation calculated for **11a**; (b) B3-P86/6-31G*-optimized bond lengths (in Å) for **11a**; (c) B3-P86/6-31G*-optimized bond lengths for naphthalene molecule; (d) atom numbering used in the text for **11a**

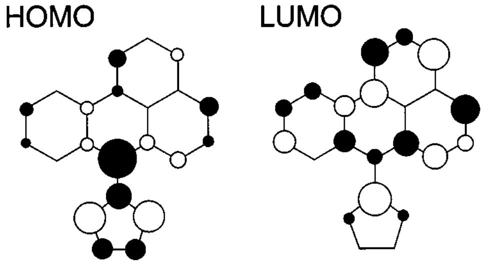


Figure 2. Atomic orbital (AO) compositions of the HOMO and LUMO of **11a**

2-ylidene subunit (−5.77 eV) and that of the HOMO of TTF (−5.09 eV). The destabilization of the HOMO on going from 1,3-dithiol-2-ylidene to **11** can be attributed to the antibonding interaction that exists between C-17 and C-9/C-12. This destabilization partly accounts for the fact that compounds **11**, even though they contain only one dithiole unit, exhibit oxidation potentials slightly higher than TTF and similar to BEDT-TTF, which contain two dithiole units.

The LUMO of **11a** extends mainly over the polyacenic skeleton and essentially corresponds to the bonding interaction of the LUMOs of the benzene and naphthalene units. The AO composition of the HOMO and the LUMO therefore indicates that the HOMO → LUMO electron transition corresponds to an electron transfer from the dithiole moiety acting as a donor to the polyacenic framework acting as an acceptor. This result supports the intramolecular charge-transfer nature of the lowest energy absorption band observed at $\lambda \approx 440$ nm for compounds **11** (see Table 1).

2. Oxidized 11a

To gain a deeper insight into the oxidation process, the molecular structure of **11a** in various oxidation states was optimized by means of B3-P86/6-31G* calculations. Figure 3 depicts the minimum-energy conformations calculated for the monocation and dication of **11a**, together with the optimized bond lengths. The monocation remains significantly distorted from planarity and retains the butterfly structure found for neutral **11a**. The values obtained for the average angle formed by the lateral benzene rings (159.4°) and for the tilting of the dithiole ring (29.0°) are close to those calculated for neutral **11a** (157.0° and 30.5°, respectively), indicating similarly folded structures.

More significant structural differences between **11a** and its monocation are found in the vicinity of the dithiole unit. While in **11a** the dithiole ring is bent along the S···S axis by 11.4°, in **11a**$^{+\cdot}$ it is almost planar. Such a planarization process has also been shown to take place for TTF on going from the neutral molecule to the cation,[18] and suggests that in **11a** the first electron is mainly removed from the dithiole moiety, in accord with the AO composition of the HOMO, which is mainly located on this moiety. The optimized bond lengths collected in Figure 3a for **11a**$^{+\cdot}$, however, suggest a different picture. In comparison to neutral

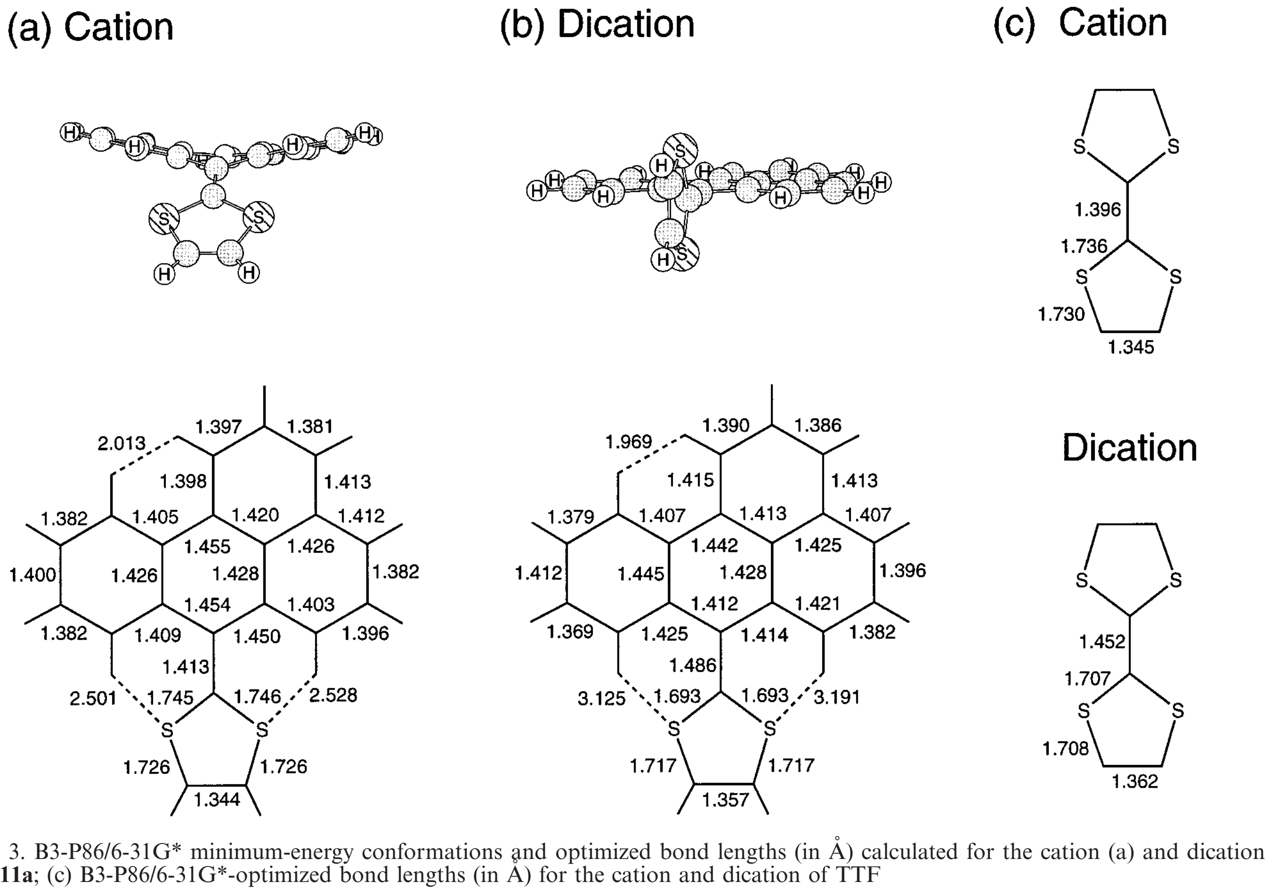


Figure 3. B3-P86/6-31G* minimum-energy conformations and optimized bond lengths (in Å) calculated for the cation (a) and dication (b) of **11a**; (c) B3-P86/6-31G*-optimized bond lengths (in Å) for the cation and dication of TTF

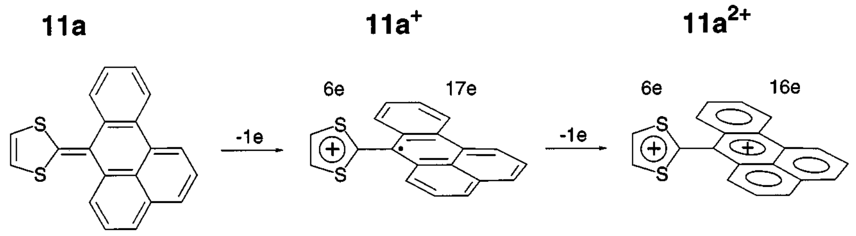


Figure 4. The oxidation process **11** → **11a**$^{2+}$ through a perpendicular structure of **11a**$^{+\cdot}$ where the dithiole ring lies orthogonal to the acene framework; the number of π-electrons on each moiety is indicated

11a (Figure 1b), the main changes are found for the C17−C18 bond length, which lengthens from 1.372 to 1.413 Å, and for the sulfur−carbon bond lengths, which shorten by 0.02−0.03 Å. However, the bonds of the acene unit are also slightly affected, suggesting that some charge is extracted from this moiety. The bond lengths calculated for the dithiole ring in **11a**$^{+\cdot}$ are in fact closer to those obtained for TTF$^{+\cdot}$, where each dithiole ring bears a charge of +1/2e, than to those found for TTF^{2+}, where each dithiole ring supports a charge of +1e (cf. Figures 3a and 3c). These structural trends are in agreement with the charge distributions calculated for **11a** and **11a**$^{+\cdot}$, which indicate that 0.42e is removed from the dithiole unit and the remaining 0.58e from the acene unit.

The extraction of the second electron to form the dication drastically affects the molecular structure of **11a**. As shown in Figure 3b, the polyacenic unit is completely planar and the dithiole ring lies perpendicular to the acene plane. This planarization is made possible by a lengthening of the exocyclic C17−C18 bond, which exhibits marked single-bond character (1.486 Å) and allows rotation of the dithiole ring out of the acene plane, thereby avoiding steric interactions between the sulfur atoms and hydrogen atoms in the *peri* positions. The resulting geometry for the dithiole moiety in **11a**$^{2+}$ is similar to that found for the dithiole rings in TTF^{2+} (cf. Figures 3b and 3c), in accord with the fact that 0.82e is removed from the dithiole unit on going from **11a** to **11a**$^{2+}$.

Theoretical results therefore indicate that both the first and second electrons are extracted from the dithiole and the polyacenic units. As depicted in Figure 4, if the first electron were to be removed wholly from the dithiole ring, we would obtain an aromatic dithiole ring having 6 π-electrons, which would be oriented perpendicularly to the neutral polyacenic unit having an odd number (17) of π-electrons. This perpendicular conformation was optimized for **11a**$^{+\cdot}$ and was found to be 6.86 kcal/mol higher in energy than the butterfly structure depicted in Figure 3. Thus, the cation preferentially adopts a charge-delocalized butterfly structure rather than a perpendicular structure with the charge localized on the dithiole ring. The contributions from both the dithiole and acene units in donating the first electron can be fully understood by considering the radical acene unit that would result if the charge-localized perpendicular structure were to be obtained. We have performed calculations on this unit by substituting the positively charged dithiole ring by a hydrogen atom. The unpaired electron lies on the non-bonding molecular orbital depicted in Figure 5, which has maximum spin density on C17 and an energy of −5.02 eV. This energy is higher than that found for the HOMO of **11a** (−5.40 eV), indicating that the resulting acene radical in perpendicular **11a**$^{+\cdot}$ should be an even better donor than neutral **11a**.

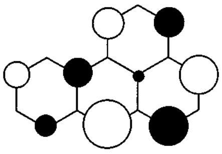


Figure 5. AO composition calculated for the HOMO of the acene unit of **11a**

In contrast to the monocation, the dication consists of two singly charged aromatic units: the dithiole ring having 6 π-electrons and the closed-shell acene moiety that now has 16 π-electrons. The molecule therefore gains in aromaticity on going from the monocation to the dication, which accounts for the small differences observed between the first two oxidation potentials for compounds **11** (see Table 1). The stability that the resulting high aromaticity confers upon the dication also explains the irreversible electrochemical behaviour observed experimentally in that the reduction (**11**$^{2+}$ → **11**) implies a marked conformational change accompanied by a loss of aromaticity in the two constituent units.

Finally, we discuss the formation of more highly charged species from compounds **11** since, as discussed above, these substrates undergo a third oxidation process to form the trication at the relatively low potential of 1.40 V (Table 1). As concluded above, the dication **11a**$^{2+}$ is made up of two singly charged, closed-shell units. Since these units lie in perpendicular planes, their interactions are minimized and they can be expected to behave as quasi-independent π-electronic units. This is illustrated in Figure 6, which shows the AO composition calculated for the HOMO of **11a**$^{2+}$. The HOMO extends over the polyacenic backbone, but there is no contribution from the dithiole ring. The topology of the HOMO therefore suggests that removal of the third electron so as to form **11a**$^{3+}$ should occur from the acene moiety. To corroborate this, the geometry of **11a**$^{3+}$ was fully optimized using the same methodological approach. The dithiole ring was found to accommodate an extra charge of only 0.10e compared to the dication, the remaining 0.90e being removed from the polyacenic unit. Thus, it can be concluded that the third oxidation process of compounds **11** corresponds to the formation of the dication of the acene unit.

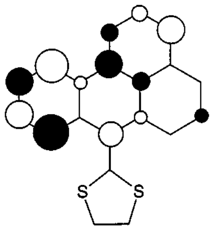


Figure 6. AO composition of the HOMO of $\mathbf{11a}^{2+}$

The electrochemical behaviour of compounds **11** thus differs drastically from that shown by extended TTFs such as **6** and **7**. Although both sets of compounds give rise to three oxidation processes at similar potential values, the assignment of these processes is completely different. For **6** and **7**, the first two processes correspond to oxidation of the dithiole rings, while the third relates to oxidation of the acene unit.[8a] In the case of **11**, the former processes correspond to the simultaneous oxidation of the unique dithiole ring and of the acene unit, while the latter is associated with the extraction of a second electron from the acene unit. That similar oxidation potentials are observed for both kinds of compounds can be attributed to the good donor properties of the acene unit in **11**, which forms highly stable cations and allows the extraction of the second electron at relatively low potentials.

Summary and Conclusions

We have designed and synthesized a new type of electron-donor molecules (**11a−c**) bearing a 1,3-dithiole ring conjugated with an acene moiety. The CV data indicate a good donor ability, similar to that of the well-known BEDT-TTF molecule. The oxidation potential values differ markedly from those shown by the individual components (1,3-dithiole and benz[*d*,*e*]anthracene), thus indicating an effective interaction between the two components. Stable CT complexes with a 2:3 stoichiometry have been prepared by mixing donors **11** with strong acceptor molecules such as $TCNQF_4$ and DDQ.

The neutral molecule adopts a butterfly-shaped nonplanar structure, which is retained in the monocation. The first electron is removed from both the dithiole ring and the polyacenic unit. In order to form the dication, the second electron is also extracted from both units, but induces a drastic change in the molecular structure. The dication is fully aromatic and consists of a closed-shell, singly-charged, planar polyacenic unit and a singly charged dithiole ring lying perpendicular to the acene plane. This high aromaticity accounts for the coalescence of the first two oxidation potentials. In forming the trication, the third electron is shown to be removed from the acene unit and thus corresponds to the second oxidation of this unit.

Experimental Section

General: ^1H- and ^{13}C-NMR spectra were recorded with a Varian VXR 300 spectrometer. − Mass spectra were measured using an HP 5989 A spectrometer operating at 70 eV. − IR spectra were recorded using a Perkin−Elmer 781 spectrometer. − Melting points were obtained using a Microlab apparatus and are uncorrected. − Cyclic voltammetry measurements were made with an EG&G PAR Versastat potentiostat using Electrochemical Analysis 250 software. A Metrohm 6.0804.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies (1×10^{-5} M solutions of the compound in dichloromethane, 0.1 M Bu_4NClO_4 as the supporting electrode, platinum working and counterelectrode, SCE as reference electrode at 20°C). − All chromatography was carried out on Merck silica gel (70−230 mesh). − All reagents were used as purchased unless otherwise stated. Solvents were dried according to standard procedures. All reactions were carried out under dry argon. 7*H*-Benz[*d*,*e*]anthracen-7-one (**10**) and *n*-butyllithium (1.6 M) were obtained commercially. Phosphonate esters **8a−c** were prepared according to previously reported procedures.[10]

Computational Details: The calculations were performed using the GAUSSIAN 94[19] system of programs on IBM RS/6000 workstations as well as with an SGI Power Challenge L R8000 computer. All calculations were carried out at the DFT level using the hybrid, gradient-corrected B3P86 density functional[20] and the 6-31G* basis set,[21] which includes polarization *d* functions on sulfur and carbon atoms. Calculations on cations and trications were performed using a spin-unrestricted formalism and a spin multiplicity value of 2. The Berny analytical gradient method[22] was used in all geometry optimizations. The requested convergence on the density matrix was 10^{-8} and the threshold values for the maximum force and the maximum displacement were 0.00045 and 0.0018 atomic units, respectively.

Wittig−Horner Reactions. − General Procedure: To a solution of the appropriate phosphonate ester **8b−c** (1 mmol) in dry THF (20 mL) at −78°C under argon, *n*BuLi (1.6 M, 1.1 mmol) was added by means of a syringe. After 30 min at −78°C, a solution of 7*H*-benz[*d*,*e*]anthracen-7-one (0.5 mmol) in dry THF (20 mL) was added to the solution of the phosphonate carbanion, also by means of a syringe. The mixture was stirred for 1 h at −78°C, then allowed to warm to 20°C and left to stand for about 12 h. The THF was subsequently evaporated under reduced pressure, water (75 mL) was added, and the residue was extracted with CH_2Cl_2 (3×75 mL). The combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The products were purified by column chromatography on silica gel using hexane/dichloromethane as eluent.

7-(1,3-Dithiol-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11a): See ref.[8b]

7-(4,5-Dimethylthio-1,3-dithiol-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11b): 78% yield; m.p. > 250°C. − $C_{22}H_{16}S_4$ (408.6): calcd. C 64.97, H 3.95; found C 65.28, H 4.32. − EI MS; *m*/*z*: 408 [M^+] (100). − ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.12 (d, *J* = 7.3 Hz, 1 H), 8.08 (m, 1 H), 7.79 (d, *J* = 7.8 Hz, 1 H), 7.71 (m, 2 H), 7.60 (m, 2 H), 7.44−7.37 (m, 3 H), 2.36 (s, 3 H), 2.34 (s, 3 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 134.1, 133.0, 132.7, 131.2, 130.2, 127.4, 127.3, 127.1, 127.0, 126.7, 126.2, 125.9, 125.2, 124.4, 124.3, 123.5, 119.4, 19.0. − IR (KBr): $\tilde{\nu}$ = 1590, 1490, 1470, 1430, 1370, 1315, 1265, 970, 895, 835, 780 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 438 (4.06), 322 (3.79), 248 nm (4.45).

7-(1,3-Dithiol-4,5-ethylenedithio-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11c): 75% yield; m.p. > 250°C. − $C_{22}H_{14}S_4$ (406.6):

calcd. C 64.99, H 3.47; found C 65.43, H 3.19. − EI MS; *m/z*: 406 (70%). − ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.07 (d, *J* = 7.5 Hz, 1 H), 8.02 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.57−7.48 (m, 2 H), 7.37 (m, 2 H), 7.27 (dd, ^1J = 8.0, ^2J = 2.0 Hz, 1 H), 3.21 (s, 2 H). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 134.2, 133.1, 132.6, 131.4, 131.2, 130.1, 127.4, 127.3, 127.1, 126.5, 126.3, 126.2, 125.1, 125.0, 124.7, 124.4, 123.4, 119.5, 111.8, 109.9, 29.5, 29.4. − IR (KBr): ṽ = 1590, 1560, 1485, 1460, 1300, 1265, 810, 780 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (log ε) = 446 (4.04), 336 (3.83), 234 nm (4.44).

Synthesis of Charge-Transfer Complexes. − General Procedure: To a boiling solution of the appropriate donor **11a**,**c** (0.1 mmol) in dry CH$_2$Cl$_2$ (10 mL) under argon was added a solution of the chosen acceptor (TCNQF$_4$ or DDQ) (0.4 mmol). The resulting dark-blue solution was refluxed for 30 min and then slowly cooled to 0°C. The solid complex that precipitated was collected by filtration, washed with cold CH$_2$Cl$_2$ (3 × 5 mL), and dried in vacuo.

7-(1,3-Dithiol-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11a)·TCNQF$_4$ Complex (2:3:1 D/A/CH$_2$Cl$_2$ Stoichiometry): 33% yield. − C$_{77}$H$_{26}$Cl$_2$F$_{12}$N$_{12}$S$_4$ (1546.2): calcd. C 59.91, H 2.11, N 10.87; found C 60.49, H 1.70, N 10.81. − IR (KBr): ṽ = 2194, 2175, 1537, 1497, 1487, 1391, 1347, 1337, 1199, 1142, 969, 769, 735, 718 cm^{-1}. − UV/vis (CH$_2$Cl$_2$): λ$_{max}$ = 862, 842, 757, 389 nm.

7-(1,3-Dithiol-4,5-ethylenedithio-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11c)·TCNQF$_4$ Complex (2:3:1 D/A/CH$_2$Cl$_2$ Stoichiometry): 35% yield. − C$_{81}$H$_{30}$Cl$_2$F$_{12}$N$_{12}$S$_8$ (1726.6): calcd. C 56.35, H 1.75, N 9.73; found C 56.67, H 2.06, N 9.39. − IR (KBr): ṽ = 2192, 2171, 1497, 1485, 1389, 1341, 1320, 1295, 1240, 967, 762 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 862, 844, 753, 394 nm.

7-(1,3-Dithiol-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11a)·DDQ Complex (2:3:2 D/A/CH$_2$Cl$_2$ Stoichiometry): 29% yield. − C$_{66}$H$_{28}$Cl$_{10}$N$_6$O$_6$S$_4$ (1483.7): calcd. C 53.43, H 2.33, N 6.15; found C 53.43, H 1.90, N 5.70. − IR (KBr): ṽ = 2225, 1629, 1578, 1559, 1452, 1385, 1354, 1278, 1245, 1197, 1080, 892, 761 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 468, 418, 354, 232 nm.

7-(1,3-Dithiol-4,5-ethylenedithio-2-ylidene)-7-hydrobenz[*d*,*e*]anthracene (11c)·DDQ Complex (2:3:1 D/A/CH$_2$Cl$_2$ Stoichiometry): 37% yield. − C$_{69}$H$_{30}$Cl$_8$N$_6$O$_6$S$_8$ (1579.1): calcd. C 51.33, H 1.83, N 10.88; found C 51.08, H 2.15, N 10.68. − IR (KBr): ṽ = 2225, 1625, 1577, 1559, 1444, 1408, 1385, 1352, 1288, 1260, 1220, 1196, 1168, 1121, 1080, 910, 890, 760 cm^{-1}. − UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ = 456, 426, 354, 232 nm.

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