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New 1,3-dithiol-2-ylidene donor–π–acceptor chromophores with intramolecular charge-transfer properties, and related donor–π–donor molecules: synthesis, electrochemistry, X-ray crystal structures, non-linear optical properties and theoretical calculations

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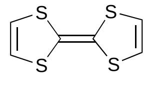
New donor–π–acceptor chromophores **5a–c**, **7a–c**, **8a–c**, **13a–c** and **14b–c** have been synthesised: substituted 1,3-dithiole derivatives span a range of donor abilities [*viz.* 4,5-dimethyl > 4,5-bis(methylsulfanyl) > 4,5-bis(methoxycarbonyl)], a conjugated ethylenic or oligoethylenic linker varies the central π-electron unit (one, two and four conjugated double bonds) and dicyanomethylene and *N*-cyanoimine groups are the acceptor units. Extended tetrathiafulvalene derivatives **15a–c** have also been synthesised. The electronic absorption spectra of compounds **5**, **7**, **8** and **14** reveal a broad low-energy intramolecular charge-transfer band [λ_{max}(MeCN) 354–533 nm] which shifts bathochromically with increasing donor strength of the dithiole ring, and with increasing length of the conjugative pathway. The solution redox properties of **5**, **7**, **8** and **14**, studied by cyclic voltammetry, reveal a reversible one-electron oxidation wave, attributed to the formation of the radical cation of the 1,3-dithiol-2-ylidene moiety, and an irreversible one-electron reduction to form the radical anion located on the dicyanomethylene or *N*-cyanoimine groups. For the bis(dithiole) donors **15a–c** a single two-electron redox wave is observed. The non-linear optical (NLO) properties of **7a–c** and **14b** have been determined using the EFISH technique: moderate NLO properties are observed for compounds **7a–c** [$\mu.\beta(0)$ 85–112 × 10^{-48} esu] whereas for the more extensively conjugated compound **14b**, the value is increased to $\mu.\beta(0)$ 1170 × 10^{-48} esu. The molecular structure and electronic properties of the unsubstituted (R = H) compounds **7**, **8**, **14** and **15** have been calculated within the density functional theory approach. The minimum energy conformation corresponds to the *trans* orientation of the side chain for **7**, and the *cis* orientation for **8**, in agreement with X-ray crystal structures and solution NMR data. The redox properties and electronic spectra are discussed on the basis of molecular orbital energies and topologies. The X-ray crystal structures of compounds **7b**, **8b** and **15b** are reported. In **7b** the 1,3-dithiol-2-ylidene and dicyanopropene systems are planar and form an angle of 3° between each other; the 'butadiene' unit has a *trans* configuration. Molecule **8b** is planar (with the exception of the methyl groups) and the imine nitrogen atom is in a *syn* orientation towards the dithiole group, forming a short intramolecular S···N contact [2.719(6) Å]. For both **7b** and **8b** π-delocalisation is observed within the central conjugated spacer unit. Molecule **15b** has a predominantly planar structure, with the central tetraene unit in an all-*trans* configuration.

Asymmetric conjugated molecules containing electron donor and electron acceptor substituents (D–π–A) have been thoroughly explored in the design of materials having highly efficient second-order non-linear optical (NLO) chromophores.[1] A prototypical example is 4-nitroaniline. Molecular non-linearity ($\beta\mu$) of such compounds is dependent on the effective length of π-conjugation and the strength of the donor and acceptor substituents. Whilst a wide variety of acceptor groups have been examined for their role in influencing the molecular NLO properties, relatively few electron donor moieties have continued to receive the most attention (*e.g.* dialkylamino and alkoxy groups). In the search for other electron donating groups we focus in this paper on derivatives of the 1,3-dithiole heterocycle. This ring system has, to date, received limited attention as a donor component in D–π–A materials. This is surprising since it has been the centre of studies within the field of organic molecular metals, as it is a constituent part of the well known π-donor tetrathiafulvalene (TTF) **1**, and the synthesis and electrochemistry of 1,3-dithiole derivatives is well developed and understood.[2] The use of the 1,3-dithiol-2-ylidene group as an electron donor has been reported previously by Gompper *et al.*,[3] and by Katz *et al.*[4] in their investigations of benzenoid type non-linear optical chromophores. Lehn and co-workers[5] have also employed the 1,3-benzodithiol-2-ylidene group in their studies on push–pull carotenoids. Jen *et al.*[6] have discussed the role of a number of 1,3-dithiol-2-ylidene derivatives in thiophene derived chromophores. Baudy-Floc'h and co-workers[7] have studied the NLO properties of some 2-imino-4-amino-1,3-dithioles and Wegner and co-workers[8] have



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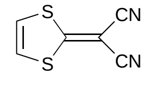

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incorporated a substituted benzo-1,3-dithiol-2-ylidenedicyanomethylene unit into the backbone of a main-chain polymer. During the preparation of this manuscript, other groups have reported new 1,3-dithiole–π–A systems.[9]

To date, very little attention has been given to the potentially important interplay that functionality on the 1,3-dithiole ring may have in modulating the degree of intramolecular charge-transfer in D–π–A materials. With this in mind, we have synthesised a range of novel D–π–A structures, varying the D, π and A fragments: substituted 1,3-dithiol-2-ylidene derivatives span a range of donor abilities [*viz.* 4,5-dimethyl > 4,5-bis(methylsulfanyl) > 4,5-bis(methoxycarbonyl)], a conjugated ethylenic or oligoethylenic linker varies the central π-electron unit (one, two and four conjugated double bonds) and the dicyanomethylene and *N*-cyanoimine groups have provided the acceptor functionality.[10]

Results and Discussion

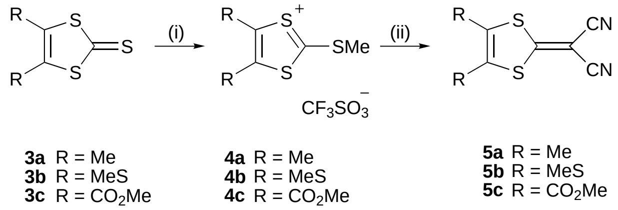
Synthesis of 5a–c, 7a–c, 8a–c, 13a–c and 14b–c

The first, and one of the simplest, D–π–A compounds utilising a 1,3-dithiol-2-ylidene donor, compound **2**,[11] was prepared by Mayer *et al.* during early pioneering investigations of the chemistry of the 1,3-dithiolium cation.[12] Using a similar procedure, we have now synthesised derivatives **5a–c** (Scheme 1). Thus, methylation of 1,3-dithiole-2-thiones **3a**,[13] **3b**[14] and **3c**[15] with methyl trifluoromethanesulfonate afforded 1,3-dithiolium cations **4a–c** (93–97%), which on reaction with malononitrile using pyridine as base gave, after spontaneous elimination of methanethiol, compounds **5a–c** (61–67% yields). We next targeted compounds **7a–c** with an additional double bond in the spacer unit. These were readily prepared in 64–71% yields by reaction of Lehnert's reagent (malononitrile, titanium tetrachloride and pyridine)[16] with the known aldehydes **6a**,[17] **6b**[18] and **6c**[17] in refluxing dichloromethane (Scheme 2). Similarly, the reaction of aldehydes **6a–c** with *N*,*N*-bis(trimethylsilyl)carbodiimide and titanium tetrachloride (according to the conditions developed by Aumüller and Hünig[19]) in dichloromethane at room temperature resulted in the formation of the corresponding *N*-cyanoimine derivatives **8a–c** (78–85%).

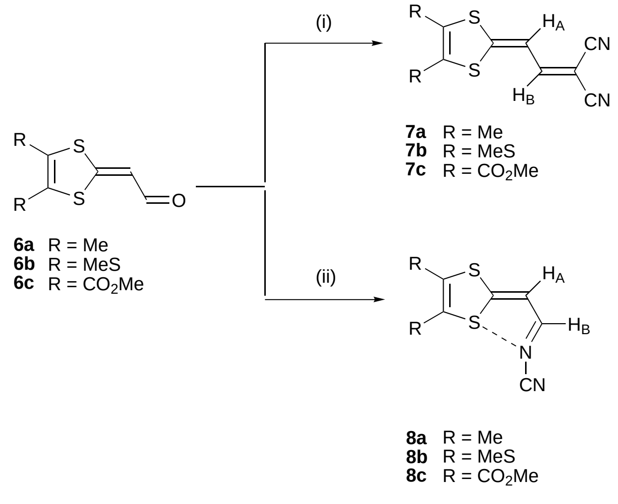
Malealdehyde **9**, which can be prepared in a high state of purity by the oxidation of furan with distilled dimethyldioxirane (DMD) in acetone,[20] has been efficiently intercepted in Wittig reactions.[21] In particular, *in situ* reaction with one equivalent of triphenylphosphoranylideneacetaldehyde afforded, after work-up and isomerisation (induced either thermally or by treatment with iodine), (*E*,*E*)-mucondialdehyde **10**[22] (62%) (Scheme 3). Compounds **14b** and **14c** were conveniently prepared in a two-step procedure from compound **10**. Compound **10** was first condensed with ylides **12a–c** (generated *in situ* from phosphonium salts **11a**,[17] **11b**[18] and **11c**[23] in tetrahydrofuran by addition of triethylamine) to afford compounds **13a–c** (54–79% yields). Compounds **13a** and **13b** were the only isolated products, even when an excess of ylides **12a** and **12b** was used in this reaction, whereas the extended bis(1,3-dithiole) donor **15c** (14%) was isolated along with compound **13c** (54%) when one equivalent of ylide **12c** was employed (see below). Subsequent reaction of compounds **13b** and **13c** with Lehnert's reagent (as described above) afforded compounds **14b** and **14c** (43 and 87% yield, respectively). Surprisingly, compound **14a** could not be obtained by this procedure. Attempts at reacting compounds **13a–c** with *N*,*N*-bis(trimethylsilyl)carbodiimide and titanium tetrachloride in dichloromethane (as above for compounds **6a–c**) gave only unchanged starting aldehydes.

Synthesis of bis(1,3-dithiol-2-ylidene)hexa-2,4-diene derivatives 15a–c

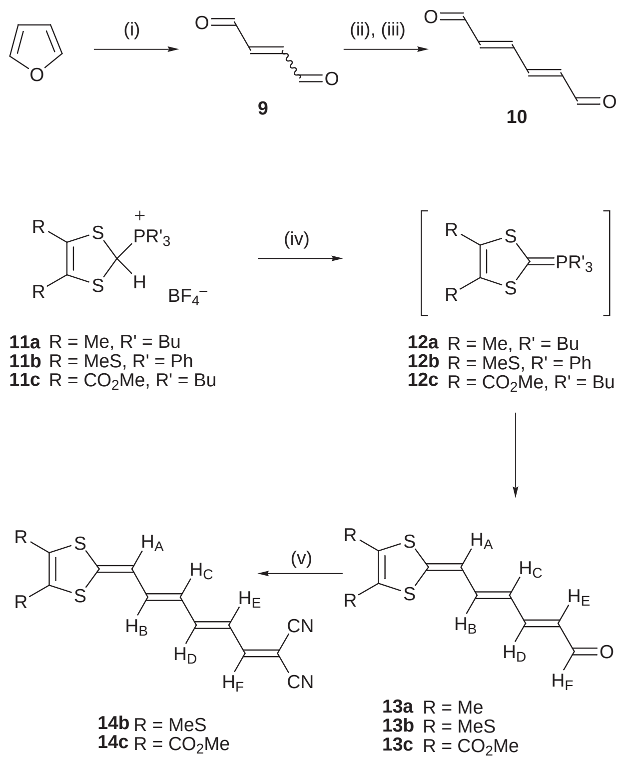
The incorporation of conjugated linking groups between the 1,3-dithiole rings of TTF has been widely explored as a structural modification of the π-donor unit. In parti-



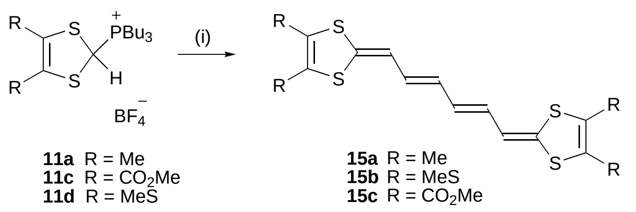
Scheme 1 *Reagents and conditions:* (i) CF_3SO_3Me, CH_2Cl_2, 20 °C, 2 h; (ii) $H_2C(CN)_2$, pyridine, Pr^iOH, 20 °C, 3 h



Scheme 2 *Reagents and conditions:* (i) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 24 h; (ii) $Me_3SiNCNSiMe_3$, $TiCl_4$, pyridine, CH_2Cl_2, 20 °C, 48 h



Scheme 3 *Reagents and conditions:* (i) DMD, acetone, 0 °C, 0.5 h; (ii) $Ph_3PCHCHO$, CH_2Cl_2, 0→20 °C, 3 h; (iii) I_2, CH_2Cl_2, 20 °C, 0.5 h; (iv) **10**, NEt_3, THF, 20 °C, 24 h; (v) $CH_2(CN)_2$, $TiCl_4$, pyridine, CH_2Cl_2, reflux, 24 h

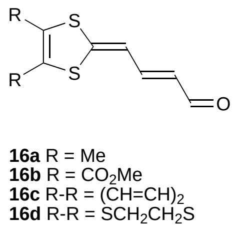


Scheme 4 *Reagents and conditions:* (i) (a) For compound **15a**: LDA, **13a**, THF, $-78 \rightarrow 20\,°C$, 16 h; (b) for compounds **15b** and **15c**: **10**, NEt_3, THF, 20 °C, 24 h

cular, olefinic,[24] quinonoid[25] and heterocyclic[26] spacers have attracted considerable attention and extensively conjugated derivatives are of interest in the context of organic molecular wires.[27] The rationale behind the design of TTF derivatives with extended conjugation is that the oxidised states responsible for conduction in charge-transfer complexes and radical cation salts should be stabilised by decreased intramolecular Coulombic repulsion. As a continuation of our interest in extended π-donors[24d,f,j,25a] and having a ready supply of dialdehyde **10**, we were attracted to the target compounds **15a–c**. As noted above, reaction of equimolar amounts of the ylide derived from phosphonium salt **11c** and dialdehyde **10** afforded both the desired aldehyde **13c** and the bis(1,3-dithiole) derivative **15c** (54 and 14% yields, respectively). Reaction of 2.5 equivalents of phosphorane **12c** with **10** increased the yield of **15c** (66%, aldehyde **13c** was also isolated in 14% yield). Similar reactions of dialdehyde **10** with up to 4 equivalents of phosphoranes **12a** and **12b** gave only aldehydes **13a** and **13b** as the isolated products (45 and 70% yields, respectively). Using the more reactive ylide derived from tributylphosphonium salt **11d**[28] (2.5 equivalents) in this reaction gave extended donor derivative **15b** in 68% yield (along with aldehyde **13b**, 18%). The tetramethyl analogue **15a** was obtained (40%) by the deprotonation of Wittig reagent **11a** in THF at −78 °C using LDA as base, following the known literature procedure,[17,24a] in the presence of aldehyde **13a** (Scheme 4).

^1H NMR Spectra of compounds 7, 8, 14 and 15

Previous structural studies on 1,3-dithiole derivatives,[29] 1,2-dithiole derivatives[30] and trithiapentalene analogues[31] bearing substituents capable of strong intramolecular $S\cdots X$ ($X = O, S$) interactions have shown they exist in a favoured s-*cis* conformation. Comparison of the ^1H NMR spectra for compounds **7a–c** and **8a–c** suggested that, in solution, compounds **7a–c** adopt very different conformations from compounds **8a–c**. In the former series, the presence of large $^3J_{AB}$ coupling (12.5–12.8 Hz) is indicative of an s-*trans* conformation; in contrast, compounds **8a–c** exhibited a significantly smaller $^3J_{AB}$ coupling (4.8–4.9 Hz) suggesting an s-*cis* conformation which could be stabilised by a close $S\cdots N$ intramolecular contact (for the solid-state structures of **7b** and **8b** determined by X-ray analysis, see below). In solution, the ethylenic chain in compounds **13a–c** and **14a–c** retains an all s-*trans* conformation; this was established by analysis of the coupling constants $^3J_{BC}$, $^3J_{DE} = 13.9$–15.1 Hz and $^3J_{AB}$, $^3J_{CD}$, $^3J_{EF} =$ 8.0–11.6 Hz. COSEY (^1H, ^1H) spectra for compounds **13a–c** and **14a–c** allowed definitive identification of all the ethylenic protons. After completion of our work, a similar synthesis of analogues **16a–d** was described by Gorgues and co-workers,[24k] for which comparable ^1H NMR data were obtained, and they too concluded an all *trans* configuration in solution. Confirmation of the all s-*trans* configuration was obtained by X-ray analysis of compound **16a**.[24k] Evidence for the retention of the all *trans* stereochemistry of dialdehyde **10** in the product **15b** obtained therefrom was provided by ^1H NMR simulation. The absolute values of proton shifts were determined by (^1H, 13C) HETCOR and, using literature *J* values, the spectra for an $(ABC)_2$ spin system were simulated using LAOCOON software and good agreement with the experimental data was found.[32] Definitive confirmation of the all *trans* stereochemistry of compound **15b** was provided by X-ray analysis (see below).



X-Ray molecular structures of compounds 7b, 8b and 15b

The single crystal structures of compounds **7b**, **8b** and **15b** have been determined by X-ray diffraction (Table 1). In molecule **7b** (Fig. 1) the dithiol-2-ylidene and dicyanopropene systems are planar and form an angle of 3° between each other. The torsion angles around the C(2)–S(3) and C(3)–S(4) bonds are 7 and 86°, respectively. Thus all the non-hydrogen atoms, except C(10), are approximately coplanar and all the multiple bonds and sulfur atoms [except S(4)] can participate in π-conjugation. The 'butadiene' moiety has a *trans*-configuration; the formally single C(4)–C(5) bond is only 0.016 Å (4σ) longer than the formally double bonds. Thus, the system is much closer to a cyanine (bond-equivalent) structure, than to genuine all-*trans* polyenes with the mean alternation (Δ) between single and double bond lengths of 0.10–0.12 Å.[33] Such

Table 1 Crystal data

compound	7b	8b	15b
formula	$C_{10}H_8N_2S_4$	$C_8H_8N_2S_4$	$C_{16}H_{18}S_8$
M	284.42	260.40	466.78
symmetry	triclinic	orthorhombic	monoclinic
a/Å	5.062(1)	15.791(1)	9.808(2)
b/Å	9.144(3)	8.140(1)	7.575(2)
c/Å	14.051(5)	8.878(1)	14.090(3)
α (°)	85.75(3)	90	90
β (°)	83.24(3)	90	93.92(2)
γ (°)	87.92(2)	90	90
U/Å^3	643.8(3)	1141.2(2)	1044.4(4)
T/K	150	150	150
radiation	Mo-Kα	Mo-Kα	Cu-Kα
λ/Å	0.71073	0.71073	1.54184
Space group	$P\bar{1}$ (No. 2)	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)
Z	2	4	2
μ/cm^{-1}	7.1	7.9	78.9
D_c/g cm^{-3}	1.47	1.52	1.48
crystal size/mm	0.1 × 0.4 × 0.4	0.35 × 0.16 × 0.015	0.05 × 0.3 × 0.5
scan mode	$\omega/2\theta$	ω	ω
$2\theta_{max}$ (°)	60	51.2	150
data total	3753	5636	2132
data unique	3185	1855	1888
data observed, $I > 2\sigma(I)$	2336	1491	1459
R_{int}	0.039	0.074	0.019
absorption correction	empirical[a]	numerical	empirical[a]
transmission min : max	0.94 : 1.00	0.690 : 0.988	0.32 : 1.00
no. of refined variables	177	160	113
weighting scheme, A, B[b]	0.046, 0.75	0, 2.66	0.108, 3.21
$wR(F^2)$, all data	0.073	0.149	0.191
goodness-of-fit	1.05	1.36	1.11
$R(F)$, obs. data	0.038	0.056	0.072
$\Delta\rho_{max}$/e Å^{-3}	0.55	0.44	0.89
$\Delta\rho_{min}$/e Å^{-3}	−0.54	−0.37	−0.52

[a] 72 ψ-scans of 2 reflections, TEXSAN software.[43] [b] $w^{-1} = \sigma^2(F^2) + (AP)^2 + BP$, where $P = (F_o^2 + 2F_c^2)/3$

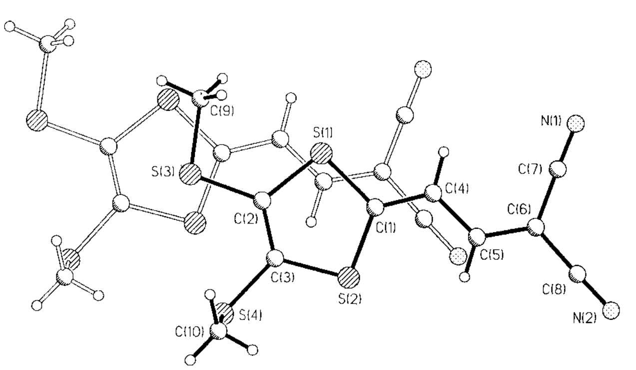
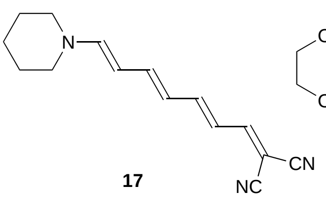


Fig. 1 Molecular structure of **7b** showing overlap of adjacent molecules in a stack. Bond distances (Å): C(1)–C(4) 1.387, C(4)–C(5) 1.402, C(5)–C(6) 1.384, C(1)–S(1) 1.743, C(1)–S(2) 1.727, S(1)–C(2) 1.757, S(2)–C(3) 1.753, C(2)–C(3) 1.343, mean C–S(Me) 1.813, C(6)–C(N) 1.430, C–N 1.149 (e.s.d. 0.004, for C–S 0.003).

a degree of π-delocalisation ($\Delta \leqslant 0.02$ Å) is usual for polyene chains with an electron-withdrawing dicyanomethylene group of one end and an electron-releasing (*e.g.* amino) substituent at the other end (*e.g.* compounds **17** and **18**).[34] 1,2-Dithiole and 1,3-dithiole heterocycles have been shown to produce a similar effect, *e.g.* compounds **19** ($\Delta = 0.02$ Å)[35] and **20**,[36] the latter having the same conjugated path and the same acceptor group as **7b**, with the same Δ value (0.016 Å). Molecules in the crystal of **7b**, related *via* an *x* translation, form a stack with an interplanar separation of *ca.* 3.4 Å and a lateral shift of 3.5 Å, such that the oppositely charged dithiole and dicyanomethylene moieties (arising as a result of intramolecular electron transfer) of adjacent molecules are nearly overlapping (Fig. 1).



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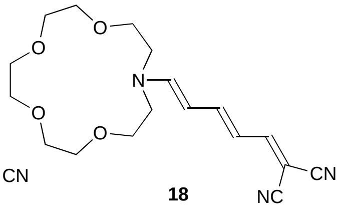

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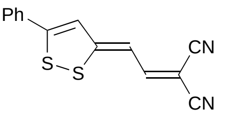

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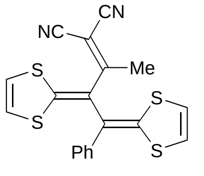

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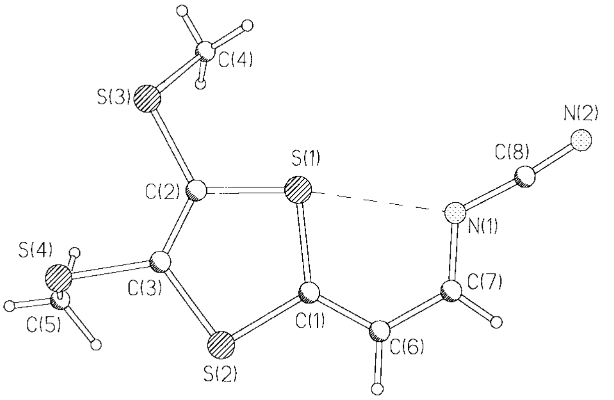


Fig. 2 Molecular structure of **8b**. Bond distances (Å): S(1)–C(1) 1.739(7), S(1)–C(2) 1.751(7), S(1)···N(1) 2.719(6), S(2)–C(1) 1.741(7), S(2)–C(3) 1.743(8), N(1)–C(8) 1.340(9), C(1)–C(6) 1.376(10), C(6)–C(7) 1.398(10), N(1)–C(7) 1.313(9), C(8)–N(2) 1.148(9); angles (°): C(2)S(1)N(1) 171.4(2), C(7)N(1)C(8) 119.8(6).

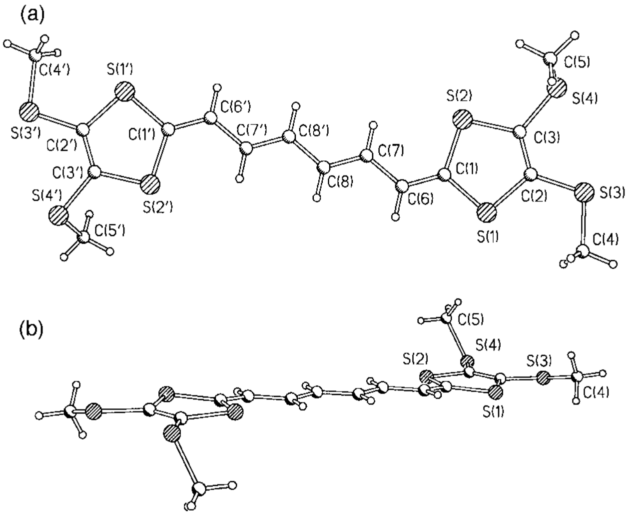
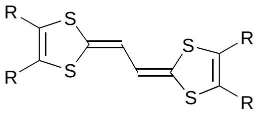


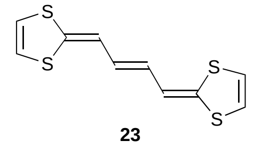
Fig. 3 (a) Molecular structure of **15b** (primed atoms are inversion-related). Bond distances (Å): C(1)–C(6) 1.348(9), C(6)–C(7) 1.430(10), C(7)–C(8) 1.369(9), C(8)–C(8′) 1.417(13), C(1)–S(1) 1.749(7), C(1)–S(2) 1.769(6), S(1)–C(2) 1.770(6), S(2)–C(3) 1.771(6), C(2)–C(3) 1.332(8). (b) Molecular structure of **15b**, side-view, showing planarity.

In molecule **8b** (Fig. 2) all non-hydrogen atoms lie in one plane within 0.03 Å, except the methyl atoms C(4) and C(5) which are situated at 1.24 and 1.67 Å, respectively, from this plane (on the same side). The N(1) atom, which is in a *syn*-orientation towards the dithiole group, forms a short intramolecular contact of 2.719(6) Å with S(1) which is substantially less than the sum of their respective van der Waals radii (3.35 Å).[37] This fact, together with π-delocalisation along the C(1)C(6)C(7)N(1) chain, suggests some degree of intramolecular sulfur···nitrogen bonding interaction. The only noteworthy intermolecular contact N(2)···S(2) ($x - 1/2, 2 - y, z$) which is nearly coplanar with the ring and *trans* to the S(2)–C(3) bond, is not particularly short (3.28 Å).

The central tetraene moiety of compound **15b** adopts an all-*trans* configuration [Fig. 3(a)]. It is notable that the alternation of bond lengths is smaller ($\Delta = 0.07$ Å) than in non-substituted octatetraene ($\Delta = 0.12$ Å).[33a] Molecule **15b** lies on a crystallographic inversion centre and has a predominantly planar structure [Fig. 3(b)], distorted by: (i) small twists (5°) around the C(6)–C(7) bond; (ii) folding of the dithiole rings along the S(1)···S(2) vectors by 8°; and (iii) out-of-plane conformation of the methyl groups, *i.e.* twists around the C(2)–S(3) and C(3)–S(4) bonds by 18 and 64°, respectively. Molecules in the crystal contact in a perpendicular edge-to-face fashion and thus no stacks exist (*cf.* extended donor **21** which stacks in uniform fashion along the *x*-axis[24j]).



21 R = MeS
22 R = H



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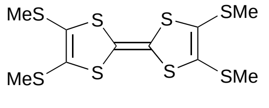

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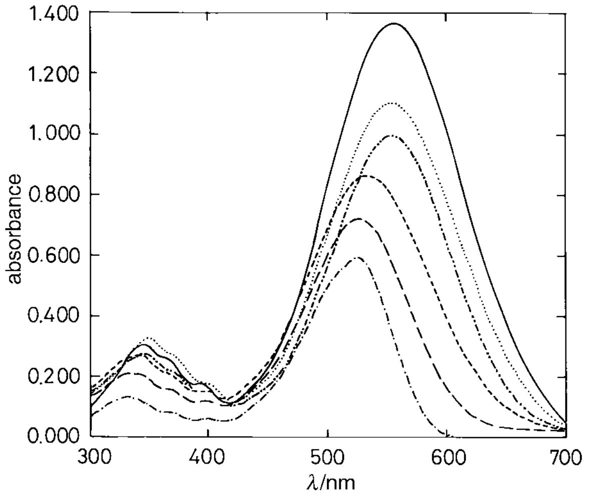

Fig. 4 UV–Visible absorption spectra for compound **14b** in various solvents, at 20 °C, demonstrating solvatochromism. Solvents: CF_3CH_2OH (——) λ_{max} 556 nm, DMSO (......) λ_{max} 553 nm, CH_2Cl_2 (-·-·-) λ_{max} 555 nm, MeCN (-----) λ_{max} 533 nm, Et_2O (— — —) λ_{max} 528 nm, hexane (-·-·-·-) λ_{max} 526 nm.

Electronic absorption spectra of compounds 5, 7, 8 and 14

The electronic absorption spectra of compounds **5**, **7**, **8** and **14** are dominated by a broad low-energy band [λ_{max}(MeCN) 354–533 nm, dependent on substituents and conjugative length (Table 2)]. Following precedents for other D–π–A systems, this band is attributed to a photoinduced intramolecular electron transfer from the 1,3-dithiol-2-ylidene moiety to the acceptor fragment. For each series of compounds **5**, **7**, **8** and **14**, the variation of donor substitution has a small, but significant, effect on the position of the charge-transfer band. In all cases, the absorption maxima in the 1,3-dithiole series shift bathochromically with increased donor strength [*e.g.* λ_{max}(MeCN) **7a** 489; **7b** 475; **7c** 439 nm]. Similarly, a comparison of absorption spectra for compounds **5b**, **7b** and **14b** shows that the maxima shift bathochromically with increasing number of conjugated double bonds [λ_{max}(MeCN) **5b** 364; **7b** 475; **14b** 533 nm]. The absorption spectra of compounds **14b** and **14c** exhibit marked solvatochromism (exemplified in Fig. 4 for compound **14b**).

Cyclic voltammetry of compounds 5, 7, 8, 14 and 15

The solution redox properties of D–π–A compounds **5**, **7**, **8** and **14** have been studied by cyclic voltammetry and the results are collated in Table 2. All the new compounds display a reversible one-electron oxidation wave, attributed to the formation of the radical cation of the 1,3-dithiole donor moiety, and an irreversible one-electron reduction wave, to form the radical anion located on the dicyanomethylene or *N*-cyanoimine group. Within each series of D–π–A systems studied (*e.g.* compounds **7a–c**) there is a small cathodic shift of both the oxidation and the reduction peaks with increasing donor strength. Similarly, when series **5**, **7** and **14** are compared, there is a significant cathodic shift in the oxidation wave and an anodic shift in the reduction wave on increasing the conjugation length (Fig. 5). The UV and CV data are entirely consistent with an increase in electron delocalisation with increasing conjugated chain length. Furthermore, they confirm that the relative donor and acceptor strenths follow the series: 4,5-dimethyl > 4,5-bis(methylsufanyl) > 4,5-bis(methoxycarbonyl) and dicyanomethylene > *N*-cyanoimine.

Table 2 Cyclic voltammetric data[a] and electronic absorption maxima[b] for D–π–A compounds **5a–c**, **7a–c**, **8a–c** and **14b–c**

	E_{ox}/V	E_{red}/V	λ_{max}/nm
5a	1.70	−1.67	387
5b	1.76	−1.52	364
5c	2.15	−1.24	354
7a	1.09	−1.18	489
7b	1.14	−1.06	475
7c	1.49	−1.01	439
8a	1.25	−1.37	450
8b	1.17	−1.22	448
8c	1.65	−1.14	426
14b	0.73	−0.84	533
14c	0.97	−0.81	492

[a] 10^{-5} M compound in dry MeCN under argon *vs.* Ag/AgCl, Pt working and counter electrodes, 20 °C, 100 mV s^{-1} scan rate. [b] In MeCN solution, 20 °C.

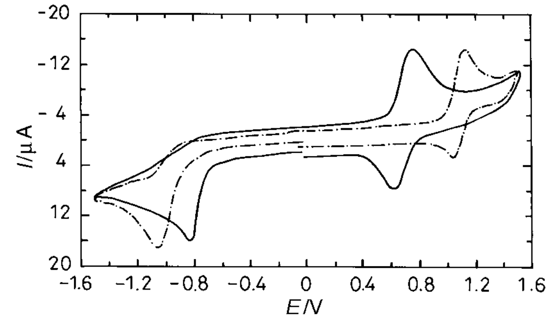

Fig. 5 Cyclic voltammograms of compounds **7b** (-·-·-·) and **14b** (——)

The solution redox properties of the bis(1,3-dithiole) donors **15a–c** are collated in Table 3, along with selected model compounds **21–24** for comparison. For all the new extended donors, only one redox couple involving a two-electron transfer is observed [this redox couple could not be resolved into two separate couples by: (i) lowering the polarity of the solvent; (ii) reducing the scan rate; (iii) lowering the temperature to −78 °C; or (iv) differential pulse voltammetry]. It is unclear whether this wave is the result of two inseparable one-electron oxidations, or a concomitant two-electron transfer. In either case, these data are entirely consistent with previous work with vinylogous TTF systems[17,24] which has established the following general trends in the redox properties with increasing conjugative length. There is: (i) a lowering of the first oxidation potential (E_1) due to the increased electron delocalisation; and, (ii) a smaller difference (ΔE) between $E_1^{1/2}$ and $E_2^{1/2}$ (tending to zero as the conjugation length increases), indicative of increased stabilisation of the dicationic state as a result of increased charge separation (and thus reduced on-site Coulombic repulsion). These observations on the influence of conjugative chain length are shown clearly in a comparison of the cyclic voltammograms of compounds **156**, **21** and **24** (Fig. 6). Predictably, compound **15a** is the best donor in the series due to the presence of the electron releasing methyl substituents on the 1,3-dithiole ring.

Table 3 Cyclic voltammetric data[a] for extended TTF vinylogues **15a–c**, with the data for compounds **1** and **21–24** for comparison

	$E_1^{1/2}$/V	$E_2^{1/2}$/V	$E_2^{1/2} - E_1^{1/2}$/V
TTF **1**	0.34	0.71	0.37
22[17]	0.20	0.36	0.16
23[17]	0.217	0.223	0.006
24	0.53	0.78	0.25
21[18,24j]	0.50	0.63	0.12
15a	0.18[b]	—	—
15b	0.36[b]	—	—
15c	0.56[b]	—	—

[a] 10^{-5} M compound in dry MeCN under argon *vs.* Ag/AgCl, Pt working and counter electrodes, 20 °C, 100 mV s^{-1} scan rate. [b] Two electron redox couple with peaks observed as a single wave, $E_{ox} - E_{red} = 56$ mV, indicative of two non-interacting redox centres

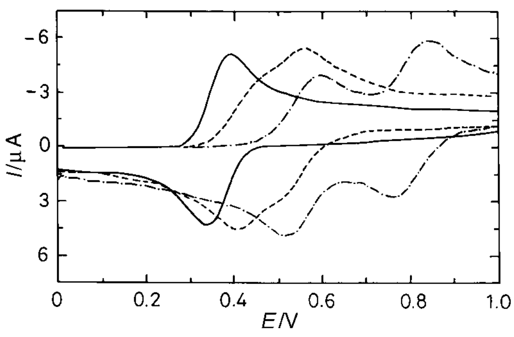

Fig. 6 Cyclic voltammograms of compounds **15b** (——), **21** (-----) and **24** (-·-·)

Table 4 Dipole moment and non-linear optical data[a]

compound	λ_0/nm	μ/D	$\beta/10^{-30}$ esu	$\beta(0)$/ 10^{-30} esu	$\mu.\beta(0)$/ 10^{-48} esu
7a	489	8.8	31	13	112
7b	475	6.9	37	15	105
7c	439	6.8	24	12	85
14b	556	—	$\mu.\beta = 4554$	—	1170

[a]Measured in $CHCl_3$. Relative errors: $\mu < 3\%$; $\beta < 10\%$; $\beta(0) < 10\%$.

Non-linear optical properties

The non-linear optical properties of compounds **7a–c** and **14b** were determined using the EFISH technique performed at 1.34 μm and the data are presented in Table 4. From experimental β values at 1.34 μm it is possible to infer 'static' $\beta(0)$ values using a two-level dispersion model,[38] which can be considered as valid in the present case of unidimensional electronic charge-transfer molecules:[39]

$$\beta = \frac{3\hbar^2}{2mW^3}\frac{W^4}{(W^2-\hbar^2\omega^2)(W^2-4\hbar^2\omega^2)}f\Delta\mu = \frac{W^4}{(W^2-\hbar^2\omega^2)(W^2-4\hbar^2\omega^2)}\beta(0) \qquad (1)$$

where

$$\beta(0) = \beta_0 = \frac{3\hbar^2}{2m}\frac{f\Delta\mu}{W^3} \qquad (2)$$

W being the energy of the charge transfer electronic transition, f the corresponding oscillator strength, $\Delta\mu = \mu_1 - \mu_0$ (where μ_1 is the dipole moment of the first excited state).

Compounds **7a–c** exhibit moderate non-linear optical properties [*cf.* the relevant application parameter is $\mu.\beta(0)$, the standard value for the 'classical' NLO dye DR1 is *ca.* 500×10^{-48} esu] (Table 4). The dependence of $\beta(0)$ upon the nature of R substitution is weak, $\mu.\beta(0)$ being slightly smaller for the weakly electron donating CO_2Me substituent. The $\beta(0)$ values are comparable to those of *p*-nitroaniline derivatives. The quadratic hyperpolarisability dramatically increases when adding two double bonds, leading to $\mu.\beta(0)$ values that are double those of the standard dye DR1. Although the dipole moment of **14b** could not be measured (due to a moderate solubility in non-polar solvents), μ was estimated to be *ca.* 7 D. This enhancement of $\mu.\beta(0)$ is strongly correlated with the increase in electron delocalisation with increasing the conjugated length. The strong red-shift of the maximum absorption wavelength λ_{max} corresponds to a significant decrease of W. The large solvatochromism of compound **14b** indicates a high $\Delta\mu$ value, and the strong hyperchromic effect observed when increasing the number of double bonds corresponds to a high oscillator strength f. All these factors result in the observed enhancement of $\mu.\beta(0)$ (by a factor of two) for compound **14b**.

Theoretical calculations

To gain a deeper understanding of the experimental trends reported above, the molecular structure and electronic properties of the unsubstituted (R = H) compounds **7**, **8**, **14** and **15** were calculated within the density functional theory (DFT) approach.[40] Compared to Hartree–Fock (HF) methods, DFT-based calculations have the advantage of including electron correlation effects and have been shown to provide more accurate optimised geometries and energetic data.[41] All calculations were performed using the B3P86 density functional and the polarised 6-31G* basis set.

Molecular structure of 7, 8, 14 and 15 (R = H). The molecular structures of **7** and **8** were optimised both in *cis* and *trans* conformations. The minimum energy conformation corresponds to the *trans* orientation for **7** and to the *cis* structure for **8** in agreement with NMR and X-ray observations. The optimised bond lengths and bond angles calculated for these structures are shown in Fig. 7. In order to compare the optimised structures with those obtained experimentally, the average deviations between the experimental X-ray data reported for **7b** and **8b** and the theoretical structures obtained for unsubstituted **7** and **8** were calculated for the bond lengths, $\bar{\delta}(R)$, and the bond angles, $\bar{\delta}(\alpha)$. The deviations were found to be very small both for **7** [$\bar{\delta}(R) = 0.012$ Å, $\bar{\delta}(\alpha) = 0.7°$] and **8** [$\bar{\delta}(R) = 0.009$ Å, $\bar{\delta}(\alpha) = 0.5°$], demonstrating the agreement between theory and experiment.

The *cis* conformer of **7** was found to be destabilised by 7.91 kcal mol^{-1} with respect to the *trans* structure due to the short S(2)···C(7) and S(2)···N(1) contacts resulting from the rotation around C(4)–C(5) [see Fig. 7(a)]. To alleviate these contacts, the S(2)–C(1)–C(4), C(1)–C(4)–C(5), C(4)–C(5)–C(6) and C(5)–C(6)–C(7) bond angles widen to 129.0, 134.9, 136.9 and 128.5°, respectively. These values are very much larger than those found for the *trans* conformer [see Fig. 7(b)] indicating the strain present in the *cis* conformer.

In contrast to **7**, the *cis* conformer of **8** is calculated to be more stable than the *trans* orientation by 3.85 kcal mol^{-1}. The optimised distance between S(1) and N(1) in the *cis* orientation is 2.722 Å, in very good agreement with the observed X-ray value of 2.719(6) Å. This short intramolecular contact is stabilised by the opposite charges borne by S(1) and N(1) (see Fig. 8), which give rise to a bonding electrostatic-type interaction. For the *trans* conformer, both sulfur atoms present net atomic charges of +0.34e. For the preferred *cis* conformer, the S(1) atom augments its charge to +0.43e and

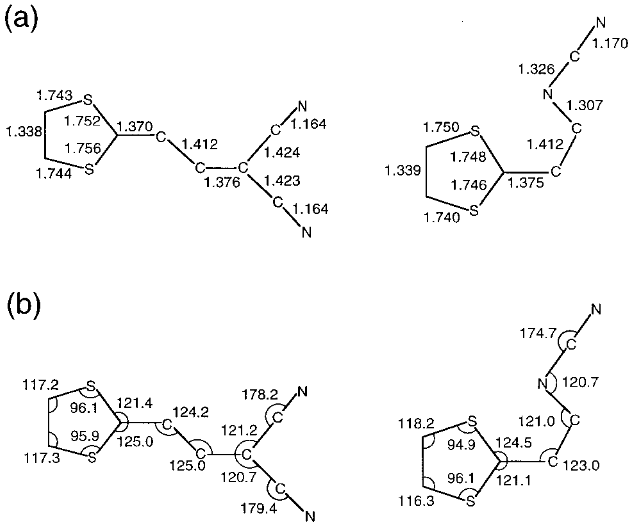

Fig. 7 B3P86/6-31G*-optimised minimum energy structures of **7** (*trans*) and **8** (*cis*). (a) Bond lengths in Å. (b) Bond angles in degrees

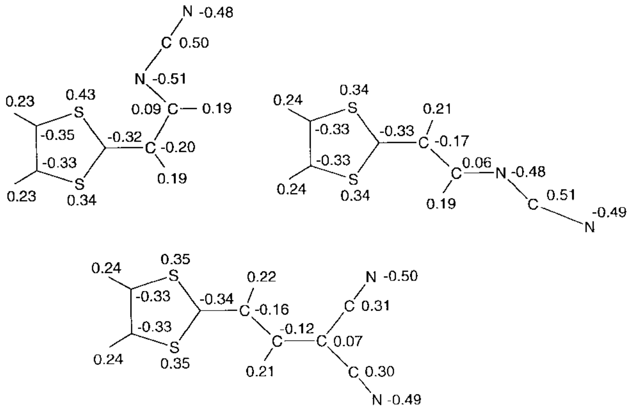

Fig. 8 B3P86/6-31G* net atomic charges (in e) for *cis* and *trans* conformations of **8** (top) and for *trans*-**7** (bottom)

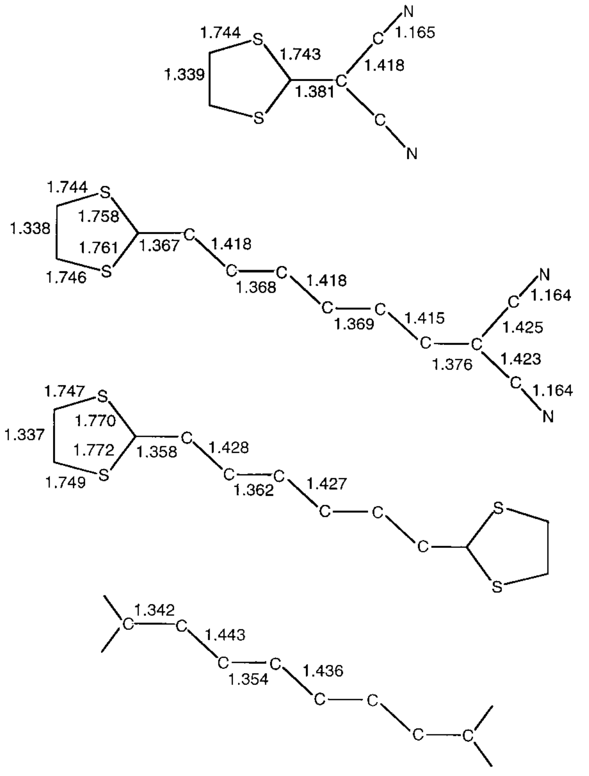

Fig. 9 B3P86/6-31G*-optimised bond lengths (in Å) of **2**, **14**, **15** and octatetraene. **2** exhibits C_{2v} symmetry. **15** and octatetraene exhibit C_{2h} symmetry.

faces the negatively charged N(1) atom (−0.51e). The adoption of a *cis* orientation by compounds **8** thus results not only in an attractive coulombic interaction, but also determines a more effective charge transfer between the donor dithiole ring and the acceptor cyanoimine unit. It should be also stressed that, for **8**, the adoption of the *cis* conformation causes no special distortion of the bond angles [see Fig. 7(b)] as was the case for *cis*-**7**. Fig. 9 shows the bond lengths calculated for unsubstituted **14** and **15** in their most stable all-*trans* conformation; the values obtained for **2** and for octatetraene are included for comparison. As the length of the conjugated linker along the series **2**, **7**, **14** increases (see Fig. 7 and 9), the mean length of the C(1)–S bonds becomes longer passing from 1.743 Å (**2**) to 1.754 Å (**7**) and to 1.760 Å (**14**). This evolution is accompanied by an increase of the mean alternation between single and double bonds in the spacer unit which varies from 0.039 Å for **7** to 0.047 Å for **14**. Both geometrical trends are a consequence of the magnitude of the electron transfer between the donor and the acceptor units. Mulliken population analysis based on B3P86/6-31G* calculations predicts that the net charge of the dithiole ring decreases in passing from **2** (+0.28e) to **7** (+0.17e) and to **14** (+0.11e). The charge transfer thus decreases as the length of the conjugated spacer increases, justifying the increase of the C(1)–S bond lengths and of the single–double bond alternation along the series **2** < **7** < **14**. However, it should be noted that although the charge transfer decreases along this series, the dipole moment increases due to the separation of the donor and the acceptor moieties. The dipole moments calculated at the B3P86/6-31G* level are 7.9 D (**2**) < 10.2 D (**7**) < 13.7 D (**14**). Although these values overestimate the experimental data for compounds **7** (see Table 4), they can be used as a good estimate of the variation of the dipole moment as the length of the conjugated spacer increases.

Compound **15** presents mean C(1)–S bond lengths of 1.771 Å and a mean alternation in the octatetraene spacer of 0.067 Å. These values are in good agreement with the experimental X-ray values (1.759 and 0.07 Å, respectively) and are larger than those theoretically obtained for **14** (1.760 and 0.047 Å). Despite the absence of charge transfer, the alternation of the conjugated spacer in **15** is significantly shorter than that calculated for the octatetraene molecule (0.101 Å) using the same theoretical approach. The terminal C(1)–C(6) and C(6)–C(7) bonds of **15** present the largest differences with the equivalent bonds of octatetraene (see Fig. 9).

Electronic structure. We turn now to discuss the redox properties on the basis of molecular orbital energies and topologies. Table 5 summarises the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **7**, **8**, **14** and **15** and of selected compounds TTF (**1**), **2**, **22** and **23** for comparison.

Table 5 B3P86/6-31G* molecular orbital energies ε

compound	ε_{HOMO}/ eV	ε_{LUMO}/ eV	compound	ε_{HOMO}/ eV	ε_{LUMO}/ eV
2	−7.07	−2.94	TTF **1**	−5.09	−1.54
7	−6.63	−3.37	**22**	−4.99	−1.35
7a	−6.37	−3.20	**23**	−4.93	−1.82
7c	−6.92	−3.53	**15**	−4.89	−2.12
8	−6.60	−2.95			
14	−6.11	−3.60			

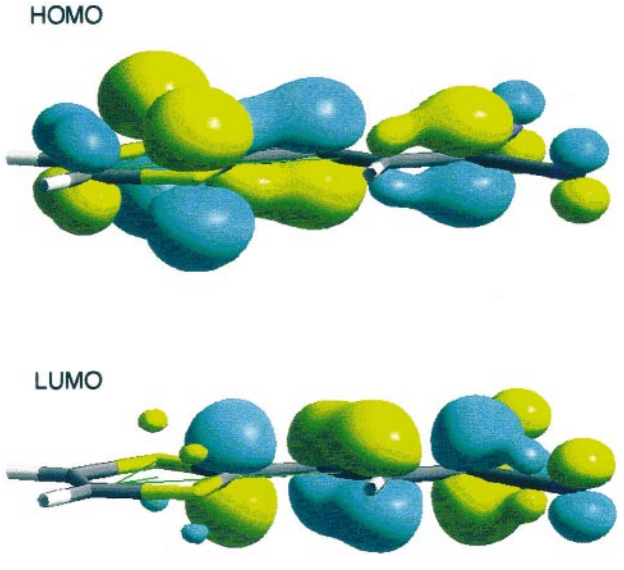

Fig. 10 Electronic density contours of the HOMO and LUMO of **7**

The topology of these orbitals is exemplified in Fig. 10 for compound **7**. The HOMO resides mainly on the 1,3-dithiol-2-ylidene group while the LUMO spreads over the C=C–C=C(CN)$_2$ unit. Similar atomic orbital compositions are found for compounds **2**, **8** and **14**.

From a MO standpoint, oxidation implies the extraction of an electron from the HOMO, and reduction implies the introduction of an electron into the LUMO. More positive oxidation potentials are therefore to be expected for compounds with lower energy HOMOs and more negative reduction potentials for compounds with higher energy LUMOs. This trend is observed when comparing the calculated MO energies (Table 5) with the redox potentials obtained experimentally by CV (Tables 2 and 3). For the D–π–A compounds, the HOMO increases in energy and the LUMO decreases in energy as the length of the conjugated π spacer increases along the series **2**, **7**, **14**. The destabilisation of the HOMO accounts for the cathodic shift of the oxidation potential and the stabilisation of the LUMO justifies the anodic shift of the reduction potential along that series. The effect of substituents has been studied for compound **7**. As the donor strength of the substituent increases [**7c** (R = CO$_2$Me) < **7** (R = H) < **7a** (R = Me)], both the energy of the HOMO [-6.92 eV < -6.63 eV < -6.37 eV] and the LUMO [-3.53 eV < -3.37 eV < -3.20 eV] increase accounting for the cathodic shift of the oxidation and reduction potentials along this series. The destabilisation effect is more important for the HOMO in agreement with the larger cathodic shifts observed for the oxidation potential (see Table 2).

The relative energies of the LUMO of **7** (-3.37 eV) and **8** (-2.95 eV) confirm the higher acceptor capability of the dicyanomethylene group in accord with CV data. The almost identical energies obtained for the HOMO of **7** (-6.63 eV) and **8** (-6.60 eV) suggest, however, that similar donor properties should be expected for both compounds. This prediction contrasts with the lower oxidation potentials measured for compounds **7**. The additional factor that should be taken into account to explain the experimental trend is the different conformations displayed by compounds **7** and **8**. As mentioned above, the *cis* conformation adopted by **8** allows for a more effective charge transfer due to the S(1)···N(1) bonding interaction. The dithiole ring exhibits a net charge of +0.23e in **8** compared to the charge of +0.17e calculated for **7**. The greater charge defect accumulated by that ring in **8** makes it harder to extract an electron upon oxidation, since it is mainly removed from the dithiole moiety, thus leading to a higher oxidation potential.

The atomic orbital composition of the HOMO and the LUMO of D–π–A compounds suggests that the lowest-energy HOMO→LUMO electronic transition implies an electron transfer from the dithiole environment to the acceptor part of the molecule. This supports the intramolecular electron transfer character of the first absorption band observed in the electronic spectra. The HOMO–LUMO energy gap decreases with the length of the conjugated spacer (**2** > **7** > **14**) and with the donor strength of the substituents (**7c** > **7** > **7a**) (see Table 5). These trends justify the bathochromic shifts observed experimentally along those series (see Table 2). The smaller values of λ_{max} measured for compounds **8** with respect to **7** are due to the higher energy of the LUMO of **8** which enlarges the HOMO–LUMO gap.

The HOMO of the bis(dithiole) compounds **22**, **23** and **15** spreads over the whole molecule involving both dithiole moieties and the central polyenic chain. This determines that its energy slightly increases with the length of the chain as is the case for polyenes. As a consequence, the first oxidation potential lowers with increasing the conjugate length (see Table 3 and Fig. 6). The LUMO decreases in energy more rapidly along the series TTF, **22**, **23**, **15** as it is localised primarily on the conjugated chain.

Conclusions

A series of novel highly-conjugated donor–π–acceptor chromophores **5a–c**, **7a–c**, **8a–c**, **13a–c** and **14b–c** have been synthesised, in which the donor units (substituted 1,3-dithioles) are separated from dicyanomethylene and *N*-cyanoimine acceptor groups by an ethylenic or oligoethylenic linker (one, two and four conjugated double bonds). Extended tetrathiafulvalene derivatives **15a–c** have also been synthesised. The electronic spectra, redox properties, non-linear optical properties and X-ray crystal structures of representative derivatives have been studied. These experimental data are supported by theoretical calculations. A broad low-energy intramolecular charge-transfer band observed for compounds **5**, **7**, **8** and **14** shifts bathochromically with increasing donor strength of the dithiole ring, and with increasing length of conjugation between the donor and acceptor moieties. Cyclic voltammetric data establish that compounds **5**, **7**, **8** and **14** undergo a reversible one-electron oxidation, and an irreversible one-electron reduction, to form the radical cation and radical anion species, respectively. For the bis(dithiole) donors **15a–c** a single two-electron redox wave is observed. Moderate NLO properties are observed for compounds **7a–c** [$\mu.\beta(0)$ 85–112 × 10^{-48} esu] whereas for the more extensively conjugated compound **14b**, the value is increased to $\mu.\beta(0)$ 1170 × 10^{-48} esu. The minimum energy conformations predicted for **7** and **8** are in agreement with X-ray crystal structures and solution NMR data. These results should stimulate further studies on the use of 1,3-dithiol-2-ylidene units as electron donor components in D–π–A materials, which by virtue of intramolecular charge-transfer will possess interesting electronic, optical, non-linear optical and structural properties.

Experimental

General methods

^{1}H NMR Spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz. ^{13}C NMR Spectra were obtained on a Varian 400 spectrometer operating at 100.581 MHz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. IR Spectra were recorded on a Perkin-Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600. UV–VIS Spectra were obtained on a Kontron Uvicon 930 spectrophotometer using quartz cells; extinction coefficients (ε) are quoted in M^{-1} cm^{-1}. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. Cyclic voltammetric data were obtained on a BAS 50W electrochemical analyser (1 × 10^{-5} M solution of donor in acetonitrile under argon, 1 × 10^{-1} M Bu$_4$NClO$_4$ supporting electrolyte, platinum working and counter electrodes, Ag/AgCl reference electrode, 20 °C). Column chromatography was performed on Merck silica gel (70–230 mesh), unless otherwise stated, and solvents were distilled prior to use. All reagents were of commercial quality and used as supplied unless otherwise stated; solvents were dried where necessary using standard procedures.

General procedure for compounds 4a–c

To a stirred solution of thiones **3a**,[13] **3b**[14] or **3c**[15] (30 mmol) in dry dichloromethane (100 ml) was added methyl trifluoromethanesulfonate (3.5 ml, 30 mmol). The resultant mixture was stirred under an argon atmosphere for 2 h at 20 °C whereupon addition of anhydrous diethyl ether (100 ml) precipitated a solid, which was filtered, washed with anhydrous diethyl ether and dried to afford the products. The products are moisture sensitive, but may be stored under argon for at least 3 months. The following were obtained.

4,5-Dimethyl-2-methylsulfanyl-1,3-dithiolium triflate 4a. (9.65 g, 96%) White solid, mp 71 °C (Analysis found: C, 26.0; H, 2.9; $C_7H_9F_3O_3S_4$ requires: C, 25.8; H, 2.8%); $\delta_H[(CD_3)_2CO]$ 3.27 (3H, s), 2.72 (6H, s).

2,4,5-Tris(methylsulfanyl)-1,3-dithiolium triflate 4b. (11.68 g, 97%) Yellow solid, mp 75 °C (Analysis found: C, 21.5; H, 2.4; $C_7H_9F_3O_3S_6$ requires: C, 21.5; H, 2.3%); $\delta_H[(CD_3)_2CO]$ 3.34 (3H, s), 2.83 (6H, s).

4,5-Bis(methoxycarbonyl)-2-methylsulfanyl-1,3-dithiolium triflate 4c. (11.88 g, 93%) White solid, mp 97 °C (Analysis found: C, 26.0; H, 2.2; $C_9H_9F_3O_7S_4$ requires: C, 26.1; H, 2.2%); $\delta_H[(CD_3)_2CO]$ 4.04 (6H, s), 3.44 (3H, s).

General procedure for compounds 5a–c

To a stirred suspension of salt **4** (15 mmol) in dry propan-2-ol (25 ml) at 20 °C under argon was first added malononitrile (1.1 g, 16.8 mmol) followed by dry pyridine (3 ml, excess). After stirring for 3 h, water (150 ml) was added and the mixture extracted into CH_2Cl_2 (3 × 75 ml) and the organic phase washed with water (2 × 200 ml). After drying ($MgSO_4$) and evaporation *in vacuo*, column chromatography eluting with CH_2Cl_2, and, if necessary, recrystallisation from $CHCl_3$ the following were obtained.

(4,5-Dimethyl-1,3-dithiol-2-ylidene)dicyanomethane 5a. (2.04 g, 67%) Tan needles, mp 228–229 °C (sublimes from *ca.* 150 °C) (Analysis found: C, 50.2; H, 2.9; N, 14.2; $C_8H_6N_2S_2$ requires: C, 49.5; H, 3.1; N, 14.4%); *m/z* (EI) 194 (M^+, 100%); *m/z* (CI) 195 ($M^+ + 1$, 25%), 212 ($M^+ + NH_4$, 100%); $\delta_H(CDCl_3)$ 2.21 (6H, s); $\delta_C[(CDCl_2)_2]$ 180.9, 129.8, 114.4, 60.7, 14.0; $\nu_{max}(KBr)/cm^{-1}$ 2205 (C≡N); $\lambda_{max}(MeCN)/nm$ (ε) 387 (1.3×10^4), 370 (1.5×40^4), 233 (4.8×10^4).

[4,5-Bis(methylsufanyl)-1,3-dithiol-2-ylidene]dicyanomethane 5b. (2.36 g, 61%) Pale yellow solid, mp 100–101 °C (Analysis found: C, 37.4; H, 2.4; N, 11.0; $C_8H_6N_2S_4$ requires: C, 37.2; H, 2.3; N, 10.8%); *m/z* (EI) 258 (M^+, 100%); *m/z* (CI) 259 ($M^+ + 1$, 50%), 276 ($M^+ + NH_4$, 100%); $\delta_H(CDCl_3)$ 2.52 (6H, s); $\nu_{max}(KBr)/cm^{-1}$ 2207; $\lambda_{max}(MeCN)/nm$ (ε) 364 (1.3×10^4), 353 (1.6×10^4), 214 (9.2×10^3).

[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]dicyanomethane 5c. (2.34 g, 65%) Cream solid, mp 104–105 °C (Analysis found: C, 42.7; H, 2.1; N, 10.0; $C_{10}H_6N_2O_4S_2$ requires: C, 42.5; H, 2.1; N, 9.9%); *m/z* (EI) 282 (M^+, 100%); *m/z* (CI) 283 ($M^+ + 1$, 40%); $\delta_H(CDCl_3)$ 3.96 (6H, s); $\delta_C[(CD_3)_2CO]$ 182.4, 161.6, 138.2, 116.7, 67.4, 59.4, 57.3; $\nu_{max}(KBr)/cm^{-1}$ 2207 (C≡N), 1710 [C(=O)–O–]; $\lambda_{max}(MeCN)/nm$ (ε) 354 (2.3×10^4), 214 (1.5×10^4).

General procedure for compounds 7a–c

To a stirred solution of aldehyde **6a**,[17] **6b**[18] or **6c**[17] (2.5 mmol) in dry CH_2Cl_2 (50 ml) under argon at 20 °C were added sequentially: (i) malononitrile (248 mg, 3.75 mmol), (ii) titanium tetrachloride (3.75 ml, 3.75 mol, 1 M in CH_2Cl_2) and (iii) dry pyridine (1 ml, excess) and the mixture was then refluxed for 24 h. After cooling, the mixture was diluted with CH_2Cl_2 (250 cm^3) and washed with water (3 × 100 ml). After drying ($MgSO_4$), the solvent was evaporated *in vacuo* and the residue was chromatographed eluting with CH_2Cl_2 to afford the products. The following were obtained.

1-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-3,3-dicyanoprop-2-ene 7a. (358 mg, 65%) Red solid, mp 222–223 °C (sublimes from *ca.* 185 °C) (Analysis found: C, 54.2; H, 3.6; N, 12.9; $C_{10}H_8N_2S_2$ requires: C, 54.5; H, 3.7; N, 12.7%); *m/z* (EI) 220 (M^+, 100%); *m/z* (CI) 221 ($M^+ + 1$, 25%), 238 ($M^+ + NH_4$, 100%); $\delta_H(CDCl_3)$ 7.35 (H_B, d, J_{AB} 12.8), 6.54 (H_A, d, J_{AB} 12.8), 2.15 (3H, s), 2.13 (3H, s); $\delta_C(CDCl_3)$ 167.3, 151.0, 127.5, 127.2, 116.0, 113.9, 106.1, 68.5, 13.7, 13.3; $\nu_{max}(KBr)/cm^{-1}$ 2208 and 2200 (both C≡N), 1540 (C=C); $\lambda_{max}(MeCN)/nm$ (ε) 489 (4.2×10^4), 467 (3.5×10^4), 249 (7.4×10^3).

1-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-3,3-dicyanoprop-2-ene 7b. (504 mg, 71%) Red solid, mp 149–150 °C (Analysis found: C, 42.2; H, 2.8; N, 9.8; $C_{10}H_8N_2S_4$ requires: C, 42.2; H, 2.8; N, 9.9%); *m/z* (CI) 285 ($M^+ + 1$, 100%), 302 ($M^+ + NH_4$, 12%); $\delta_H(CDCl_3)$ 7.30 (H_B, d, J_{AB} 12.7), 6.65 (H_A, d, J_{AB} 12.7), 2.47 (s, 3H), 2.46 (s, 3H); $\delta_C(CDCl_3)$ 164.2, 150.8, 130.8, 130.3, 115.1, 113.1, 108.0, 71.7, 19.2, 19.1; $\nu_{max}(KBr)/cm^{-1}$ 2210 (C≡N), 2198 (C≡N), 1554 (C=C); $\lambda_{max}(MeCN)/nm$ (ε) 475 (5.3×10^4), 318 (1.0×10^4), 244 (1.0×10^4). A crystal suitable for X-ray analysis was grown by slow evaporation of its CH_2Cl_2 solution.

1-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-3,3-dicyanoprop-2-ene 7c. (492 mg, 64%) Orange solid, mp 202–203 °C (sublimes from *ca.* 150 °C) (Analysis found: C, 46.9; H, 2.7; N, 9.0; $C_{12}H_8N_2O_4S_2$ requires: C, 46.8; H, 2.6; N, 9.1%); *m/z* (CI) 309 ($M^+ + 1$, 80%), 326 ($M^+ + NH_4$, 100%); $\delta_H(CDCl_3)$ 7.32 (H_B, d, J_{AB} 12.5), 6.60 (H_A, d, J_{AB} 12.5), 3.92 (6H, s); $\nu_{max}(KBr)/cm^{-1}$ 2218 (C≡N), 2208 (C≡N), 1707 [C(=O)–O–]; $\lambda_{max}(MeCN)/nm$ (ε) 439 (2.5×10^4), 241 (5.8×10^3).

General procedure for compounds 8a–c

To a stirred solution of aldehyde **6a**[17], **6b**[18] or **6c**[17] (3 mmol) in dry CH_2Cl_2 (25 ml) under argon at 20 °C were added sequentially (i) titanium tetrachloride (3.3 ml, 3.3 mmol, 1 M in CH_2Cl_2), (ii) *N*,*N*-bis(trimethylsilyl)carbodiimide (0.75 ml, 3.3 mmol) and (iii) dry pyridine (1 ml, excess) and the mixture was stirred for a further 48 h. After dilution with CH_2Cl_2 (250 ml) the mixture was washed with water (3 × 100 ml). After drying ($MgSO_4$), the solvent was evaporated *in vacuo* and the residue was chromatographed eluting with ethyl acetate to afford the products. The following were thus obtained.

1-(*N*-Cyanoimino)-2-(4,5-dimethyl-1,3-dithiol-2-ylidene)ethane 8a. (459 mg, 78%) Orange solid, mp 181–182 °C (sublimes from *ca.* 130 °C) (Analysis found: C, 48.8; H, 3.8; N, 14.3; $C_8H_8N_2S_2$ requires: C, 49.0; H, 4.1; N, 14.3%); *m/z* (CI) 197 ($M^+ + 1$, 100%); $\delta_H(CDCl_3)$ 8.24 (H_B, d, J_{AB} 4.9), 6.39 (H_A, d, J_{AB} 4.9), 2.23 (3H, s), 2.22 ((3H, s); $\delta_C(CDCl_3)$ 167.6, 166.3, 131.9, 126.9, 118.8, 103.4, 13.5, 13.0; $\nu_{max}(KBr)/cm^{-1}$ 2155 (C≡N), 1542 (C=C), 1457 (C=N); $\lambda_{max}(MeCN)/nm$ (ε) 450 (5.0×10^4), 432 (3.7×10^4), 236 (9.7×10^3).

1-(*N*-Cyanoimino)-2-[4,5-bis(methylsufanyl)-1,3-dithiol-2-ylidene]ethane 8b. (660 mg, 85%) Orange solid, mp 127–128 °C (Analysis found: C, 37.0; H, 2.9; N, 10.9; $C_8H_8N_2S_4$ requires: C, 36.9; H, 3.1; N, 10.7%); *m/z* (CI) 261 ($M^+ + 1$, 100%); $\delta_H(CDCl_3)$ 8.32 (H_B, d, J_{AB} 4.8), 6.48 (H_A, d, J_{AB} 4.8), 2.56 (3H, s), 2.51 (3H, s); $\delta_C(CDCl_3)$ 167.3, 166.1, 134.9, 129.5, 117.9, 105.4, 19.2, 19.0; $\nu_{max}(KBr)/cm^{-1}$ 2161 (C≡N), 1540 (C=C), 1455 (C=N); $\lambda_{max}(MeCN)/nm$ (ε) 448 (1.3×10^4), 307 (2.5×10^3), 201 (8.1×10^3). A crystal suitable for X-ray analysis was grown by slow evaporation of its CH_2Cl_2 solution.

1-(*N*-Cyanoimino)-2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]ethane 8c. (681 mg, 80%) Bright yellow solid, mp 156–157 °C (Analysis found: C, 42.0; H, 2.7; N, 10.2; $C_{10}H_8N_2O_4S_2$ requires: C, 42.2; H, 2.8; N, 9.9%); *m/z* (CI) 261 ($M^+ + 1$, 100%); $\delta_H(CDCl_3)$ 8.45 (H_B, d, J_{AB} 4.9), 6.59 (H_A, d, J_{AB} 4.9), 3.95 (3H, s), 3.93 (3H, s); $\nu_{max}(KBr)/cm^{-1}$ 2189 (C≡N), 2169 (C≡N), 1733 and 1710 [both C(=O)–O], 1575 and 1559 (both C=C), 1471 (C=N); λ_{max}(MeCN)/nm (ε) 426 (3.5×10^4), 414 (3.6×10^4), 227 (1.3×10^4).

General procedure for compounds 13a–c

To a stirred solution of Wittig reagent **11a**,[17] **11b**[18] or **11c**[23] (1.5 mmol) and dialdehyde **10**[21] (1.5 mmol) in dry THF (50 ml) under argon at 20 °C was added dry triethylamine (1 ml, excess) and stirring was continued for 16 h. After evaporation of the solvent *in vacuo*, the residue was extracted with CH_2Cl_2 (250 ml) and washed with water (3 × 100 ml). The organic layer was dried ($MgSO_4$) and the solvent evaporated *in vacuo*. Purification of the products was achieved by column chromatography. The following were thus obtained.

(*E*,*E*)-6-(4,5-Dimethyl-1,3-dithiol-2-ylidene)hexa-2,4-dienal 13a. Elution with CH_2Cl_2 (150 mg, 45%) as a red solid, mp 108–110 °C (Analysis found: C, 59.0; H, 5.4; $C_{11}H_{12}OS_2$ requires: C, 58.8; H, 5.4%); *m/z* (DCI) 225 ($M^+ + 1$, 100%); δ_H($CDCl_3$), 9.50 (H_F, d, J_{EF} 8.1), 7.14 (H_D, dd, J_{DC} 11.5, J_{DE} 15.0), 6.57 (H_B, dd, J_{BA} 12.0, J_{BC} 11.2)., 6.21–6.02 (H_A, H_C, H_E, m); ν_{max}(KBr)/cm^{-1} 1667 (C=O) 1603, 1567, 1501 (all C=C); λ_{max}(MeCN)/nm (ε) 451 (1.5×10^4), 280 (9.9×10^3), 229 (6.4×10^4).

(*E*,*E*)-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]hexa-2,4-dienal 13b. Elution with CH_2Cl_2 (341 mg, 79%) as a deep red solid, mp 95–96 °C (Analysis found: C, 45.8; H, 4.4; $C_{11}H_{12}OS_4$ requires: C, 45.8; H, 4.2%); *m/z* (CI) 289 ($M^+ + 1$, 100%); δ_H($CDCl_3$) 9.52 (H_F, d, J_{EF} 8.1), 7.12 (H_D, dd, J_{DC} 11.1, J_{DE} 15.0), 6.52 (H_B, dd, J_{BA} 11.6, J_{BC} 14.1), 6.20 (H_C, dd, J_{CB} 14.1, J_{CD} 11.1), 6.13 (H_A, d, J_{AB} 11.6), 6.09 (H_E, dd, J_{ED} 15.0, J_{EF} 8.1), 2.41 (3H, s), 2.40 (3H, s); δ_C($CDCl_3$) 193.2, 152.2, 143.3, 137.5, 129.6, 127.8, 126.7, 125.4, 113.2, 19.0, 18.9; ν_{max}(KBr)/cm^{-1} 1670 (C=O), 1595 and 1573 (both C=C); λ_{max}(MeCN)/nm (ε) 438 (2.1×10^4), 293 (7.6×10^3), 229 (4.4×10^3).

(*E*,*E*)-6-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-hexa-2,4-dienal 13c. Initial elution with CH_2Cl_2 afforded compound **15c** (108 mg, 14%); continued elution with CH_2Cl_2–acetone mixture (10:1 v/v) afforded the product **13c** (252 mg, 54%) as an orange solid, mp 147–148 °C (Analysis found: C, 51.3; H, 3.7; $C_{13}H_{12}O_5S_2$ requires: C, 50.0; H, 3.9%); *m/z* (CI) 313 ($M^+ + 1$, 100%); δ_H($CDCl_3$) 9.55 (H_F, d, J_{EF} 8.0), 7.11 (H_D, dd, J_{DE} 15.1, J_{DC} 11.1), 6.47 (H_B, dd, J_{BA} 11.2, J_{BC} 14.3), 6.25 (H_C, dd, J_{CB} 14.3, J_{CD} 11.1), 6.16 (H_A, d, J_{AB} 11.2), 6.10 (H_E, dd, J_{ED} 15.1, J_{EF} 8.0), 3.86 (6H, s); ν_{max}(KBr)/cm^{-1} 1730 and 1702 [both C(=O)–O], 1664 (C=O), 1603 (C=C), 1581 (C=C); λ_{max}(MeCN)/nm (ε) 410 (2.9×10^4), 264 (8.2×10^3), 229 (7.8×10^3).

General procedure for compounds 14b–c

To a stirred solution of aldehyde **13b–c** (0.7 mmol) in dry CH_2Cl_2 (50 ml) under argon at 20 °C were added sequentially: (i) malononitrile (66 mg, 1 mmol), (ii) titanium tetrachloride (1.0 ml, 0.75 mol, 1 M in CH_2Cl_2) and (iii) dry pyridine (1 ml, excess) and the mixture was then refluxed for 24 h. After cooling, the mixture was diluted with CH_2Cl_2 (250 ml) and washed with water (3 × 100 ml). After drying ($MgSO_4$), the solvent was evaporated *in vacuo* and the residue was chromatographed to afford the products. The following were thus obtained.

(*E*,*E*)-1-[4,5-Bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-7,7-dicyanohepta-2,4,6-triene 14b. Eluting with CH_2Cl_2–hexane (2:1 v/v) (101 mg, 43%) as a deep red solid, mp 160–162 °C (Analysis found: C, 50.1; H, 3.7; N, 8.2; $C_{14}H_{12}N_2S_4$ requires: C, 50.0; H, 3.6; N, 8.3%); *m/z* (CI) 337 ($M^+ + 1$, 100%; δ_H($CDCl_3$) 7.42 (H_F, d, J_{EF} 11.9), 6.95 (H_D, dd, J_{DC} 11.5, J_{DE} 14.1), 6.65 (H_E, dd, J_{ED} 14.1, J_{EF} 11.9), 6.55 (H_B, dd, J_{BA} 11.6, J_{BC} 13.9), 6.24 (H_A, d, J_{AB} 11.6), 6.18 (H_C, dd, J_{CB} 13.9, J_{CD} 11.5), 2.45 (3H, s), 2.43 (3H, s); ν_{max}(KBr)/cm^{-1} 2215 (C≡N), 1581 (C=C); λ_{max}(MeCN)/nm (ε) 533 (2.3×10^4), 326 (6.8×10^3), 264 (6.2×10^3).

(*E*,*E*)-1-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-7,7-dicyanohepta-2,4,6-triene 14c. Eluting with CH_2Cl_2 (219 mg, 87%) as a deep red solid, mp 213–214 °C (Analysis found: C, 53.4; H, 3.5; N, 7.6; $C_{16}H_{12}N_2O_4S_2$ requires: C, 53.3; H, 3.3; N, 7.7%); *m/z* (CI) 361 ($M^+ + 1$, 100%); δ_H($CDCl_3$) 7.39 (H_F, d, J_{EF} 12.0), 6.92 (H_D, dd, J_{DC} 11.6, J_{DE} 14.1), 6.67 (H_E, dd, J_{ED} 14.1, J_{EF} 12.0), 6.50 (H_B, dd, J_{BA} 11.5, J_{BC} 13.9), 6.22 (H_A, d, J_{AB} 11.5), 6.21 (H_C, dd, J_{CB} 13.9, J_{CD} 11.6), 3.87 (6H, s); δ_C($CDCl_3$) 159.1, 159.0, 158.8, 147.9, 142.8, 138.8, 133.0, 131.1, 127.3, 125.1, 114.0, 112.1, 109.7, 79.8, 53.8, 53.7; ν_{max}(KBr)/cm^{-1} 2217 (C≡N), 1717 and 1700 [both C(=O)–O], 1566 (C=C); λ_{max}(MeCN)/nm (ε) 492 (7.5×10^4), 302 (1.0×10^4), 252 (1.0×10^4).

(*E*,*E*)-1,6-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)hexa-2,4-diene 15a

To a solution of Wittig reagent **11a**[17] (410 mg, 0.9 mmol) and aldehyde **13a** (50 mg, 0.23 mmol) in dry THF (50 ml) at −78 °C was added LDA (1 M in cyclohexane, 0.6 ml, 0.9 mmol) and the solution allowed to attain room temperature over 16 h. The solvent was evaporated and the residue extracted into toluene (100 ml), washed with water (100 ml) and the organic phase dried ($MgSO_4$). After evaporation of the solvent, the residue was chromatographed (neutral alumina, 70–230 mesh) eluting with hexane–toluene (6:1 v/v) to afford compound **15a** as a black solid (30 mg, 40%); mp 170–173 °C (Analysis found: C, 57.0; H, 5.3; $C_{14}H_{18}S_4$ requires: C, 56.8; H, 5.3%); *m/z* (DCI) 339 ($M^+ + 1$, 100%); δ_H($CDCl_3$) 6.00–5.98 (6H, m), 1.92 (6H, s) 1.89 (6H, s); λ_{max}(MeCN)/nm (ε) 476 (2.9×10^4), 452 (2.0×10^4), 270 (9.9×10^3), 215 (6.4×10^3).

General procedure for compounds 15b–c

To a stirred solution of Wittig reagent **11c**[23] or **11d**[28] (2.0 mmol) and dialdehyde **10**[21] (0.9 mmol) in dry THF (50 ml) under argon at 20 °C was added dry triethylamine (1.5 ml, excess) and stirring was continued for 16 h. After evaporation of the solvent *in vacuo* the residue was chromatographed to afford the products. The following were thus obtained.

(*E*,*E*)-1,6-Bis[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]hexa-2,4-diene 15b. Elution with CH_2Cl_2–hexane (1:1 v/v) (285 mg, 68%) as a dark orange solid, mp 165–167 °C (Analysis found: C, 41.0; H, 4.0; $C_{16}H_{18}S_8$ requires: C, 41.2; H, 3.9%); *m/z* (CI) 467 ($M^+ + 1$, 100%); δ_H($CDCl_3$) 6.05–5.85 (6H, m), 2.34 (6H, s), 2.32 (6H, s); δ_C($CDCl_3$) 132.1, 129.5, 129.0, 127.8, 126.6, 125.7, 125.5, 124.4, 124.3, 115.3, 115.1, 111.1, 18.9, 18.8; λ_{max}(MeCN)/nm (ε) 456 (2.6×10^4), 430 (2.2×10^4), 273 (8.5×10^3), 213 (8.6×10^3). A crystal suitable for X-ray analysis was grown by slow evaporation of its MeCN solution. Continued elution with CH_2Cl_2 afforded compound **13b** (47 mg, 18%).

(*E*,*E*)-1,6-Bis[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]hexa-2,4-diene 15c. Elution with CH_2Cl_2 (310 mg, 66%) as a dark orange solid, mp 186–188 °C (Analysis found: C, 46.5; H, 3.6; $C_{20}H_{18}O_8S_4$ requires: C, 46.7; H, 3.5%); *m/z* (CI) 515 ($M^+ + 1$, 100%); δ_H($CDCl_3$) 6.05–5.97 (6H, m), 3.83 (6H, s) 3.81 (6H, s); ν_{max}(KBr)/cm^{-1} 1749, 1730 and 1702 [all C(=O)–O], 1598 and 1563 (both C=C); λ_{max}(MeCN)/nm (ε) 433 (9.6×10^4), 410 (8.5×10^4), 388 (5.0×10^4), 239 (1.5×10^4). Continued elution with CH_2Cl_2–acetone (10:1 v/v) afforded compound **13c** (40 mg, 14%).

X-Ray crystallography

Single-crystal X-ray diffraction experiments were carried out on a Rigaku AFC6S 4-circle diffractometer (**7b**, **15b**) or a Siemens 3-circle SMART diffractometer with a CCD area detector (**8b**), using graphite monochromators and Oxford Cryosystems open-flow N_2 gas cooling devices. The structures were solved by direct methods and refined by full-matrix least squares against F^2 on all data, using SHELXTL software.[42] Non-H atoms were refined anisotropically; all H atoms in **7b** and **15b** were refined isotropically; in **8b** methyl groups were refined as rigid bodies, other H atoms were treated as 'riding'. Highest peaks of the residual electron density in all structures occur near sulfur atoms. Crystal data and experimental details are listed in Table 1; atomic coordinates and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/88.

Non-linear optical measurements

β Measurements were obtained in chloroform, the fundamental wavelength was 1.34 µm, and the source was a Nd^{3+} YAG Q-switched, mode-locked laser, emitting 90 ns duration pulse trains, the duration of each pulse being 160 ps. To complete these measurements the dipole moments were separately determined in chloroform solution with a WTW dipole meter coupled with an Abbe refractometer, in order to measure the relative permittivity and the refractive index of the solutions. From these experimental data the dipole moment was deduced using the Guggenheim model.[44] Static $\beta(0)$ values were deduced from the experimental values using a two-level dispersion model [eqn. (3)]

$$\beta(0) = \beta(\lambda)[1-(2\lambda_0/2\lambda)^2][1-(\lambda_0/\lambda)^2] \qquad (3)$$

(λ being the fundamental wavelength and λ_0 the first maximum absorption wavelength).

Computational details

The calculations were performed using the GAUSSIAN 94[45] system of programs on IBM RS/6000 workstations and on a SGI Power Challenge L R8000 computer at the Department of Química Física of the University of Valencia. All the calculations were carried out at the DFT level using the hybrid gradient-corrected B3P86 density functional[46] and the 6-31G* basis set,[47] which includes polarisation *d* functions on sulfur, nitrogen and carbon atoms. The Berny analytical gradient method[48] was used in all the geometry optimisations. 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. All the molecules were restricted to be planar during geometry optimisation.

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