

A novel π -donor– π -acceptor system: 1-(4,5-dimethyl-1,3-dithiol-2-ylidene)- 1-ferrocenyl-3,3-dicyanopropene

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Abstract

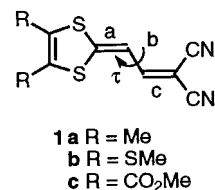
The title compound was prepared by reacting the anion of malononitrile with the corresponding ethanal, and characterised by UV–vis absorption spectroscopy, cyclic voltammetry and X-ray crystallography. Attachment of an additional ferrocenyl donor group to the π -donor– π -acceptor system does not enhance intramolecular charge transfer, because its bulk distorts the planarity of the conjugated chain. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

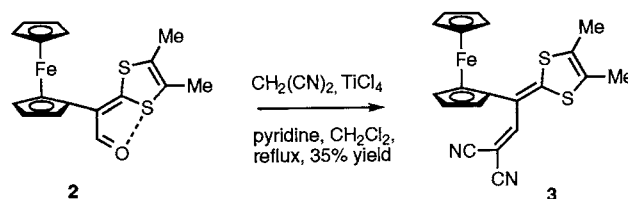
In a quest for materials that possess intramolecular charge-transfer and which may display non-linear optical (NLO) properties, molecules with π -donor and π -acceptor substituents on opposite ends of a conjugated chain (D– π -A, or push–pull systems) are of great importance [1,2]. Recently we [3] and other workers [4] have studied a number of compounds (e.g. **1a–c**) with a 1,3-dithiole ring as the π -donor and a dicyanomethylene group as the π -acceptor, which displayed moderate NLO properties. Ferrocene, like 1,3-dithiole, is an electron donor with the half-wave potential $E^{1/2} = 0.36$ V (vs. Ag/AgCl) comparable to that of tetrathiafulvalene (TTF) (0.34 V) [5], which readily forms charge-transfer complexes. A ferrocenyl group, covalently linked to a dithiole or a TTF system, has been shown to increase the stability of the cation–radical product of its oxidation [6,7]. With ferrocene derivatives easily available, it seemed timely to synthesise the first D– π -A systems containing both dithiole and ferrocenyl donor units, and to explore the effect of

this structural modification on intramolecular charge-transfer properties.



2. Results and discussion

Compound **3** was prepared from the previously reported ethanal precursor **2** [6] (Scheme 1) in 35% yield. It is notable that compound **3** is a black crystalline solid, whereas analogue **1a** is red. Thus introduction of



Scheme 1.

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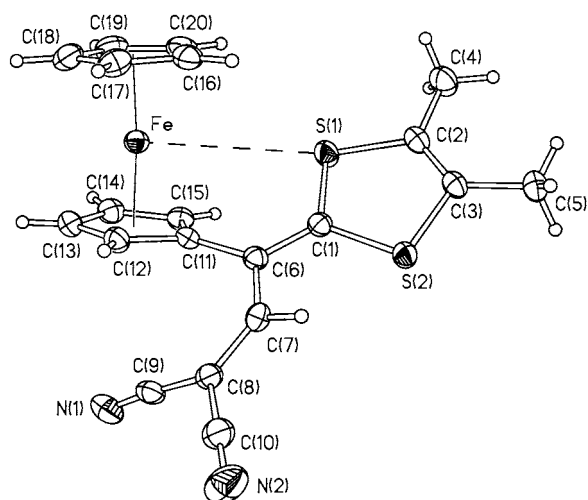
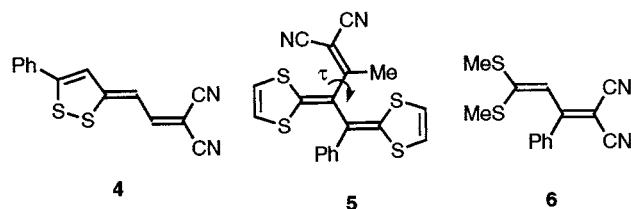


Fig. 1. Molecular structure of **3**, showing 50% displacement ellipsoids.

a ferrocenyl substituent (although formally cross-conjugated) has a profound effect on the π -electron distribution within the chromophore. The UV–vis spectrum of **3** in dichloromethane displays a sharp absorption band at λ_{max} 491 nm with a very broad, lower intensity, long-wave shoulder (extending to ca. 700 nm). The band can be attributed to a photoinduced intramolecular electron transfer from the dithiole to the dicyanomethylene moiety and does not differ significantly from the analogous band of **1a** ($\lambda_{\text{max}} = 489$ nm) [3]. Perhaps surprisingly, this absorption band is not augmented by the inductive effect of the ferrocenyl group. The origin of the shoulder is unclear.

Cyclic voltammetry of **3** in acetonitrile solution revealed a reversible oxidation wave at $E_{1/2}^{\text{ox}} = 0.48$ V (vs. Ag/AgCl) (ferrocenyl oxidation), an irreversible wave at $E^{\text{ox}} = 1.08$ V (dithiole oxidation, cf. 1.09 V for **1a** [3]) and an irreversible reduction wave at $E^{\text{red}} = -1.27$ V (cf. -1.18 for **1a**), attributable to the reduction of the dicyanomethylene unit [8].

The structure of **3**, determined by single-crystal X-ray diffraction (see Fig. 1 and Table 1), provides instructive comparisons with the known structures of **1b** [3], **4** [9], the 1,2-dithiole analogue **5** [10] and compound **6** [11]. A simple measure of intramolecular charge transfer is provided by the extent of bond alternation Δ , i.e. the average difference between the lengths of (formally) double (i and iii) and single (ii) bonds along the conjugated chain. Δ can vary from 0.11 Å in a polyene chain (with no charge transfer) to zero in a fully zwitterionic (e.g. cyanine) structure [12,13]. Naturally, deviations from planarity, particularly the twist of a butadiene moiety around the central C–C bond (torsion angle τ), reduce the delocalisation (see Table 2).



In contrast with **1b**, the D- π -A of system **3** is substantially non-planar. The dithiole ring is folded along the S(1)⋯S(2) vector by 7.9(1)°. The butadiene moiety adopts a twist $\tau = 21.3(3)$ ° around the central C(6)–C(7) bond, sufficient to interfere with the π -conjugation. The twists around the C(1)–C(6) and C(7)–C(8) bonds are also substantial, 6.7(3) and 7.4(3)°, respectively. Thus the distortion due to the bulkiness of the ferrocenyl moiety outbalances the *I*-donor effect of the latter that could enhance the charge transfer, which in the solid state structure of **3** is actually less than in **1b** and comparable to that in the non-planar **6**.

The twist of 36.1(2)° around the C(6)–C(11) bond leaves little possibility for conjugation between the cyclopentadienyl and butadiene π -systems. Due to steric overcrowding of the molecule, the S(1) atom is wedged between cyclopentadienyl rings of the sandwich moiety (perfectly at its equatorial plane), making the ring planes appreciably non-parallel, with the dihedral angle of 5.8(2)°. Although the Fe⋯S(1) distance of 3.681(1) Å is well outside the covalent bonding range, it is considerably closer than in other ferrocene–dithiole derivatives. In an excited state (e.g. during a UV–vis photolysis in the spectrometer beam) intra- and/or intermolecular interactions in **3** can be postulated, which may be responsible for the long wavelength shoulder in the UV–vis spectrum.

Table 1
Selected bond distances (Å) and angles (°)

Bond distances			
Fe–C(11)	2.085(2)	C(1)–S(2)	1.738(2)
Fe–C(12)	2.040(3)	C(2)–S(1)	1.745(2)
Fe–C(13)	2.044(3)	C(3)–S(2)	1.764(2)
Fe–C(14)	2.049(3)	C(2)–C(3)	1.758(2)
Fe–C(15)	2.065(3)	C(1)–C(6)	1.337(4)
Fe–C(16)	2.058(3)	C(6)–C(7)	1.392(3)
Fe–C(17)	2.058(3)	C(6)–C(11)	1.432(3)
Fe–C(18)	2.048(3)	C(7)–C(8)	1.484(3)
Fe–C(19)	2.048(3)	C(8)–C(9)	1.370(3)
Fe–C(20)	2.047(3)	C(8)–C(10)	1.438(4)
C–N, av.	1.149(3)	C(1)–S(2)–C(3)	1.439(4)
Bond angles			
C(1)–S(1)–C(2)	97.5(1)	C(6)–C(1)–S(2)	97.0(1)
C(6)–C(1)–S(1)	124.8(2)	C(1)–C(6)–C(7)	122.7(2)
C(6)–C(11)–C(12)	125.5(2)	C(1)–C(6)–C(11)	116.5(2)
C(6)–C(11)–C(15)	127.6(2)	C(7)–C(6)–C(11)	122.6(2)
C(12)–C(11)–C(15)	106.8(2)	C(1)–S(1)	120.9(2)

Table 2
Geometry of conjugated D- π -A molecules

Compound	1b	3	4	5	6
i (Å)	1.387(4)	1.392(3)	1.402	1.39(1)	1.365(5)
ii (Å)	1.402(4)	1.432(3)	1.413	1.40(1)	1.424(4)
iii (Å)	1.384(4)	1.370(3)	1.392	1.38(1)	1.372(4)
Δ (Å)	0.016(7)	0.051(5)	0.016	0.01(2)	0.056(8)
τ (°)	3	21.3(4)	1.4	7	19.6
Reference	[3]	This work	[9]	[10]	[11]

Future work will explore the steric and electronic effects of substituents on 1,3-dithiole- π -A chromophores with emphasis on tailoring their optoelectronic properties for device applications.

3. Experimental

Details of instrumentation and general experimental procedures are the same as those reported recently [3].

3.1. Preparation of 1-(4,5-dimethyl-1,3-dithiole-2-ylidene)-1-ferrocenyl-3,3-dicyano-propene **3**

To a stirred solution of 1-(4,5-dimethyl-1,3-dithiole-2-ylidene)-1-ferrocenyl-ethanal **2** [3] (100 mg, 0.29 mmol) in dry CH_2Cl_2 (30 ml) at room temperature were added sequentially: 1 M solution of TiCl_4 in CH_2Cl_2 (0.34 ml, 0.34 mmol), malononitrile (0.02 ml, 0.34 mmol) and pyridine (0.03 ml, 0.34 mmol). The solution was refluxed for 12 h, the solvent was evaporated in vacuo and the residue chromatographed on silica gel (eluent CH_2Cl_2), yielding **3** as a black solid (40 mg, 35%), m.p. 198–200°C (decomp.). Elemental analysis calculated for $\text{C}_{20}\text{H}_{16}\text{FeN}_2\text{S}_2$: C 59.41, H 3.99, N 6.93; Found: C 59.55, H 4.20, N 6.80. $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ , ppm: 7.49 (1H, s), 4.45–4.42 (4H, m), 4.23 (5H, s), 2.23 (6H, s). IR (cm^{-1}): 2216, 1535, 1478, 1425, 1345, 1297. UV ($\text{e M}^{-1} \text{cm}^{-1}$) in CH_2Cl_2 , λ_{max} nm: 253 (7.6×10^3), 350 (1.2×10^4), 491 (1.8×10^4). Mass spectrum, m/z (DCI): 405 ($\text{M}^+ + 1$, 100). Slow evaporation of a CH_2Cl_2 –hexane (1:1 v/v) solution of **3** yielded single crystals of X-ray quality.

The X-ray diffraction experiment was carried out at $T = 150$ K with a SMART 1K CCD area detector, mounted on a three-circle diffractometer (graphite-monochromated Mo- $\text{K}\alpha$ radiation, $\bar{\lambda} = 0.71073$ Å). Crystal data: $\text{C}_{20}\text{H}_{16}\text{FeN}_2\text{S}_2$, $M = 404.3$, monoclinic, space group $P2_1/n$ (no. 14), $a = 14.208(1)$, $b = 7.640(1)$, $c = 16.557(1)$ Å, $\beta = 95.94(1)^\circ$, $V = 1787.6(3)$ Å³ (from 502 setting reflections with $12 < \theta < 23^\circ$), $Z = 4$, $D_{\text{calc.}} = 1.50 \text{ g cm}^{-3}$, $F(000) = 832$, $\mu = 10.8 \text{ cm}^{-1}$, crystal size $0.5 \times 0.1 \times 0.1$ mm. Four sets of ω scans by 0.3° , each set at different ϕ and/or 2θ angles, nominally covered over a hemisphere of reciprocal space. Reflec-

tion intensities were integrated using SAINT software [14] and corrected for absorption by semi-empirical method based on Laue equivalents and multiple reflection measurements, using SADABS program [15] (min/max transmission factors 0.755 and 0.920). Of 9536 reflections with $2\theta \leq 54^\circ$, 3220 were unique, 2739 observed with $I \geq 2\sigma(I)$; $R_{\text{int}} = 0.030$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of 3208 data, using SHELXTL software [16]. The refinement (all non-H atoms anisotropic, all H atoms refined isotropically, 291 variables) converged at $wR(F^2) = 0.080$, $R[I \geq 2\sigma(I)] = 0.031$, goodness-of-fit 1.14, residual $\Delta\rho_{\text{max}} = 0.28$, $\Delta\rho_{\text{min}} = -0.27 \text{ e Å}^{-3}$.

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 127665 for compound **3**. Copies of the information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-maildeposit@ccdc.ac.uk or www:http://www.ccdc.cam.ac.uk).

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