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Highly polarized dithiafulvenes: synthesis and nonlinear optical properties

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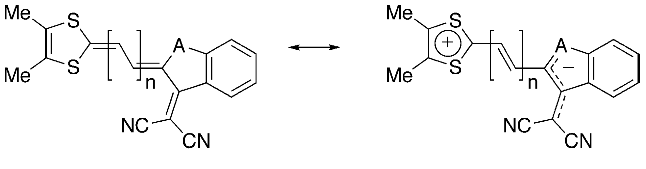
Abstract—Push–pull dithiafulvenes with reduced bond length alternation (BLA) and high optical nonlinearities have been prepared. The interplay between the proaromaticity of the donor and the structural and optical properties of these merocyanines is discussed. The donor ability of dithiafulvenes can reach that of ferrocene or dialkylaminophenyl groups.

Push–pull polyenes are at the forefront of research in the field of organic compounds showing second-order nonlinear optical (NLO) properties. For these compounds, the ground-state polarization, BLA, and ultimately, the second-order NLO properties are governed by the size and nature of the spacer, the donor–acceptor strength and the aromatic or proaromatic character of the different subunits.[1] When linked to aromatic donors, acceptors like 3-dicyanomethylenebenzo[*b*]thiophene-1,1-dioxide[2–4] and related indanedione derivatives[5] give rise to high quadratic hyperpolarizabilities ($\mu\beta$), but the linking of such acceptors to proaromatic donors has not been described yet. In this letter, we report the synthesis of merocyanines **3**, **5** and **7** bearing a 1,4-dithiafulvene donor[6] and the experimental and theoretical results correlating the structure (BLA, mixing of the limiting forms) and NLO properties of these merocyanines.



3: A = SO_2; **5**: A = CO; **7**: A = C=C(CN)$_2$

The target push–pull systems were prepared by Knoevenagel reaction of polyenals **1a**–**c**[7,8] with acceptors **2**,[9,10] **4**[11] and **6**,[11] respectively (Scheme 1). The desired merocyanines **3**,[12] **5**[13] and **7**[14] are easily purified, although the stability of **5c** in solution is very limited. Attempts to synthesize higher vinylogues of **7a** led to decomposition products.

^{1}H NMR data (see below) support the geometries depicted in Scheme 1 for merocyanines **3**, **5** and **7**, although they do not allow an unambiguous assignment of the configuration of the C=C bond exocyclic to the acceptor fragment. This configuration is tentatively assigned as (*Z*)- by analogy with other arylmethylidene systems related to **3a** and **5a**, for which X-ray data are available, that show that the aryl group is located trans to the bulky dicyanomethylene group.[15,16]

Electrochemical data of the newly prepared compounds are gathered in Table 1. All compounds show two chemically irreversible waves, corresponding to the oxidation of the dithiafulvene fragment and to the reduction of the acceptor moiety, respectively. (Compound **7a** displays additional waves at more cathodic potentials.) For a given length of the spacer, E_{ox} values decrease in the order **3** > **7** > **5**, whereas reduction of the acceptor shifts to more negative values along this series. Both of these factors indicate that the acceptor strength of the studied moieties decreases in the order **2** > **6** > **4**.[16] Moreover, lengthening the polyenic spacer gives rise to both easier oxidation and reduction processes, indicating a weaker

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Keywords: Dithiafulvenes; Proaromaticity; Nonlinear optics; Bond length alternation.

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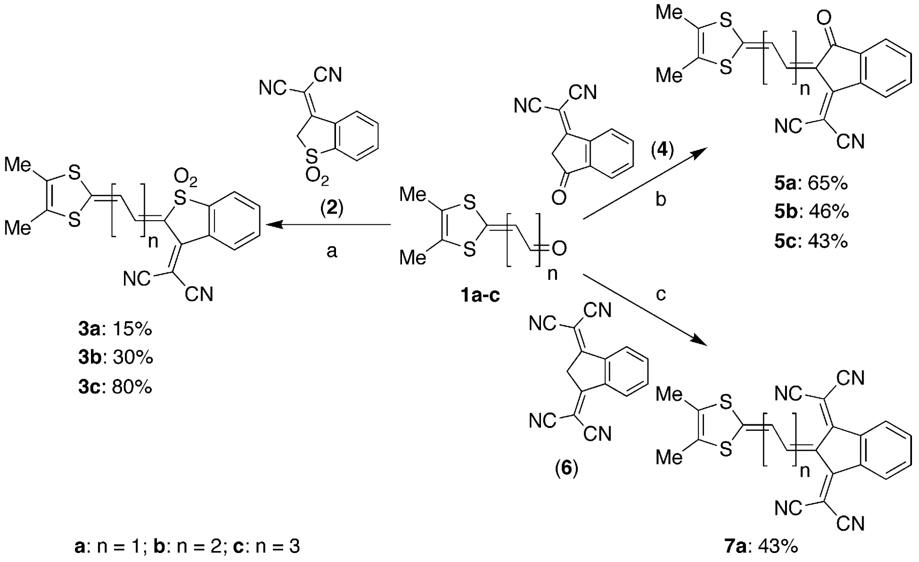


Scheme 1. Reagents and conditions: (a) EtOH, reflux, 1 h, overnight, rt; (b) EtOH, 70 °C, 1.5 h (5 h for **5c**); 1.5 h, rt; (c) Ac_2O, 70 °C, 1.5 h.

Table 1. Electrochemical, linear and nonlinear optical properties

Compound	E_{ox}[a]	E_{red}[a]	λ_{max} (lg ε)[b]	λ_{max}[c]	$\mu\beta$[d]	$\mu\beta_0$[e]
3a	1.21	−0.68	649 (4.79)	658	260	123
3b	0.92	−0.56	750 (5.06)	765	1820	587
3c	0.68	−0.48	852 (5.06)	870	3800	612
5a	1.11	−0.94	623 (4.90)	631	255	130
5b	0.82	−0.73	711 (4.98)	734	1620	620
5c	0.65	−0.69	784 ([f])	835	[f]	[f]
7a	1.17	−0.70	643 (4.57)	651	[f]	[f]

[a] E in V versus Ag/AgCl, glassy carbon working electrode, $TBAPF_6$ 0.1 M in CH_2Cl_2, 0.1 V/s.

[b] In nm, measured in CH_2Cl_2.

[c] In nm, measured in DMSO.

[d] In 10^{-48} esu, measured in CH_2Cl_2 at 1907 nm.

[e] In 10^{-48} esu, determined using the two-level model.

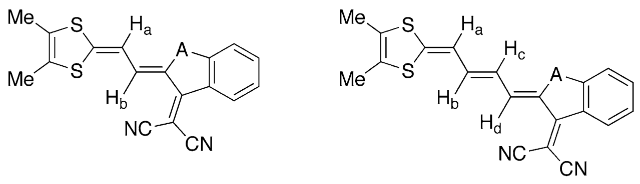
[f] Not determined due to its low solubility and/or stability.

interaction of the end groups (and, therefore, a smaller contribution of the zwitterionic form to the ground state for the longer derivatives). A similar trend has been reported for related push–pull molecules derived from acceptor **2**.[17]

All compounds show intense absorption bands in the visible or near-IR region (Table 1). Within each series there is a large vinylene shift that, for compounds **3**, amounts to about 100 nm. This behaviour is similar to that displayed by cyanine dyes[18] and is in sharp contrast to the marked hypsochromic shift shown by TTF-π-dicyanomethyleneindanone derivatives on lengthening the polyenic spacer.[19] Compound **3** are more bathochromic than **5**, which points to a stronger acceptor character of the sulfone-containing moiety **2**, when compared to acceptor **4**.[11] This is in good agreement with the cyclovoltammetric data discussed above. Concerning compound **7a**, its λ_{max} is intermediate between those of **3a** and **5a**,[16] although its molar absorption coefficient is the lowest of all three compounds, reflecting the increased steric crowding in **7a**.[11] All compounds show positive solvatochromism, indicating an increased contribution of the zwitterionic form to the excited state. This is confirmed by theoretical calculations, which show that $\mu_e > \mu_g$ (where e and g refer to the excited and ground states, respectively).

The second-order NLO properties of the NLO-phores were determined by EFISH. The $\mu\beta$ values range from 255×10^{-48} to 3800×10^{-48} esu, increasing with the conjugation length (Table 1). Measured $\mu\beta$ values for compounds **3** compare favourably to those described for similar compounds bearing a ferrocene donor unit,[20] although are substantially lower than those displayed by analogous dialkylaminophenyl derivatives.[2,3] On the other hand, $\mu\beta$ values of compounds **5** show that the donor ability of the dithiafulvenyl unit is similar to that of dialkylaminophenyl in NLO-phores of similar length incorporating polyene[21] or thienylenevinylene spacers[5] and acceptor **4**, and much larger than that of the TTF moiety[22] for a given number of conjugated atoms.

Since β values depend on the ground-state polarization and, therefore, on BLA, the evaluation of these parameters is important to understand the second-order NLO properties of the newly prepared merocyanines. $^3J_{HH}$ values in $CDCl_3$ indicate a reduced BLA along the spacer (Fig. 1).



	J_{ab}
3a	13.6
5a	12.9
7a	13.3

	J_{ab}	J_{bc}	J_{cd}
3b	12.5	12.8	12.7
5b	12.9	13.5	12.0

Figure 1. $^3J_{HH}$ values (Hz) in $CDCl_3$ along the spacer for selected merocyanines.

Table 2. Structural and nonlinear optical parameters (HF/6-31G*//B3P86/6-31G*)

Parameter	3a	3b	3c	5a	5b	5c
|BLA|[a]	0.031	0.039	0.041	0.029	0.039	0.042
C–S[b]	1.749	1.754	1.757	1.751	1.756	1.759
$\mu\beta_0$[c]	153	690	1793	152	629	1523

[a] In Å.

[b] In Å. Average C–S dithiole bond lengths adjacent to the exocyclic C=C bond.

[c] In 10^{-48} esu.

Thus, for compounds **a**, $J_{ab} \approx 13$ Hz, which indicates a substantial character of trans double bond and an important contribution of the zwitterionic form. This is further confirmed by the $^3J_{HH}$ values of compounds **3b** and **5b**, which show an average difference across adjacent bonds in the spacer of 0.2 and 1 Hz, respectively. These data point to weakly alternated structures in $CDCl_3$, even approaching the cyanine limit in **3b**.

Geometry optimizations on model compounds (where methyl substituents have been replaced by H atoms) have been performed using the B3P86/6-31G* model chemistry (Table 2) and they afford slightly more alternated structures in the gas phase, although their |BLA| values are low. It can be seen that |BLA| increases on lengthening the spacer, in good agreement with the decreased importance of the zwitterionic form (due to the higher energy needed for charge separation), already evidenced by cyclic voltammetry.

Moreover, the progressive increase along both series (**3** and **5**) in the bond lengths of the dithiole C–S bonds adjacent to the exocyclic double bond also supports the decreased charge transfer, given the susceptibility of these bonds to the charge on the dithiole moiety.[23]

Calculated $\mu\beta_0$ values (CPHF/6-31G* method on the above-mentioned geometries) are in good agreement with the experimental values, except for **3c**, the reasons for this discrepancy being not clear. The previously mentioned lower $\mu\beta$ values of compounds **3**, when compared to those displayed by analogous systems with a dialkylaminophenyl donor, can be related to the strong proaromatic character of the dithiole moiety when combined to powerful acceptors like **2**. The gain in aromaticity in **3** on charge separation gives rise to weakly alternated structures, which lie in region B, according to Marder's classification,[24] past the optimal |BLA| value. (A related situation has been found in NLO-phores derived from 5-piperidinothiophene, a stronger and less aromatic donor than its 4-dibutylaminophenyl analogue.)[3]

To sum up, we have prepared a series of highly polarized dithiafulvene-containing merocyanines. As judged from their $\mu\beta$ values, dithiafulvenes are, in some cases, as efficient as ferrocene or dialkylaminophenyl donors. On the other hand, when very strong acceptors are used, dithiafulvenes are less efficient than dialkylaminophenyl groups, since the proaromaticity of the former results in enhanced contribution of the zwitterionic form, thus shifting the corresponding compounds past the optimal BLA value.

Acknowledgements

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12. Analytical data. For **3a**: mp: 284–287 °C; IR (Nujol): 2198 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 2.22 (s, 6H), 7.16 (d, $J = 13.6$ Hz, 1H), 7.67–7.72 (m, 2H), 7.84 (dd, $J = 4.6$ Hz, $J' = 1.6$ Hz, 1H), 8.58 (d, $J = 13.6$ Hz, 1H), 8.80 (dd, $J = 4.9$ Hz, $J' = 1.9$ Hz, 1H); MS (EI): 384 ($M^{+\cdot}$). For **3b**: mp: 259–260 °C; IR (Nujol): 2194, 2175 cm^{-1}; ^1H NMR ($CDCl_3$) δ (ppm): 2.14 (s, 6H), 6.57 (d, $J = 12.5$ Hz, 1H), 6.93 (dd, $J = 12.8$ Hz, $J' = 12.7$ Hz, 1H), 7.14 (dd, $J = 12.8$ Hz, $J' = 12.5$ Hz, 1H), 7.66–7.72 (m, 2H), 7.83 (d, $J = 5.0$ Hz, 1H), 8.41 (d, $J = 12.7$ Hz, 1H), 8.78 (d, $J = 5.2$ Hz, 1H); MS (EI): 410

$(\mathrm{M}^{+\cdot})$. For **3c**: mp: 204–205 °C; IR (Nujol): 2182, 2160 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ (ppm): 2.06 (s, 6H), 6.28–6.36 (m, 2H), 6.77–6.90 (m, 2H), 7.45–7.51 (m, 1H), 7.65–7.86 (m, 3H), 8.41 (d, $J = 11.2$ Hz, 1H), 8.77 (d, $J = 7.8$ Hz, 1H); MS (EI): 434 $(\mathrm{M}^{+\cdot}-2)$.

13. Analytical data. For **5a**: mp: 301 °C; IR (Nujol): 2210, 1691 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ (ppm): 1.48 (s, 6H), 7.59–7.68 (m, 2H), 7.68–7.70 (m, 1H), 8.20 (d, $J = 12.9$ Hz, 1H), 8.40 (d, $J = 12.9$ Hz, 1H), 8.49–8.51 (m, 1H); MS (EI): 348 $(\mathrm{M}^{+\cdot})$. For **5b**: mp: 278 °C; IR (Nujol): 2207, 1675 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ (ppm): 2.12 (s, 3H), 2.15 (s, 3H), 6.55 (d, $J = 12.9$ Hz, 1H), 7.13 (dd, $J = 12.9$ Hz, $J' = 13.5$ Hz, 1H), 7.63 (m, 2H), 7.80 (d, $J = 6.6$ Hz, 1H), 7.97 (dd, $J = 12.0$ Hz, $J' = 13.5$ Hz, 1H), 8.36 (d, $J = 12.0$ Hz, 1H), 8.60 (d, $J = 6.6$ Hz, 1H); MS (EI): 374 $(\mathrm{M}^{+\cdot})$. For **5c**: mp: 187–188 °C; IR (Nujol): 2208, 1694 cm^{-1}; MS (EI): 398 $(\mathrm{M}^{+}-2)$; Anal. Found: C, 68.85; H, 3.89; N, 7.12; $\mathrm{C_{23}H_{16}N_2OS_2}$ requires: C, 68.97; H, 4.03; N, 6.99.
14. Analytical data: mp: 254–256 °C; IR (Nujol): 2210 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ (ppm): 2.23 (s, 6H), 6.65 (d, $J = 13.3$ Hz, 1H), 7.53–7.55 (m, 2H), 8.33 (d, $J = 13.3$ Hz, 1H), 8.43–8.46 (m, 2H); MS (EI): 396 $(\mathrm{M}^{+\cdot})$.
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