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Novel NLO-phores with Proaromatic Donor and Acceptor Groups

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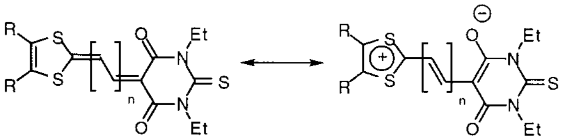
ABSTRACT



Novel D-π-A NLO-phores based on the 1,3-dithiol-2-ylidene donor and the thiobarbituric acceptor moieties have been prepared. Modification of the length and rigidity of the π-spacer allows the first systematic study of the second-order nonlinear optical properties of doubly proaromatic merocyanines. The π-electron donor efficiency of the 1,3-dithiol-2-ylidene group is superior to that of the tetrathiafulvalenyl group.

Donor (D)-acceptor (A) substituted organic molecules with large second-order nonlinear optical (NLO) properties constitute a topic of burgeoning interest due to their possible applications in areas such as frequency doubling and photorefractive polymers, among others.[1] These molecules can show large first molecular hyperpolarizabilities (β), related to an electronic intramolecular charge-transfer excitation between the ground and excited states of the molecule,[2] and it has long been recognized that D-π-A NLO-phores with a dominantly aromatic ground state do not favor electronic polarization in an applied field, as a result of the decreased resonance energy upon charge transfer.[3] This led Marder et al. to design D-π-A systems in which the loss of aromaticity in one end (D) on charge separation was offset by a gain in aromaticity in the opposite end (A).[4] Given the success of this approach to obtain NLO-phores with high β values, a great deal of effort has been devoted to the study of derivatives bearing proaromatic acceptors.[4,5]

In contrast, there are only scant reports on the NLO properties of doubly (D and A) proaromatic push−pull NLO-phores, and most of them have been carried out on isolated compounds, thus preventing the establishment of structure−property relationships.[6] In this Letter we report the first systematic experimental and theoretical study of the second-order NLO properties of merocyanines incorporating both a proaromatic donor and a proaromatic acceptor. As a proaromatic donor unit we have focused on the 1,3-dithiol-2-ylidene moiety, first used by Katz[7] and Lehn[8] in the search for new NLO-phores,[9] on account of the contribution of the aromatic 1,3-dithiolium ion to the charge-separated state; 1,3-diethylthiobarbituric acid has been chosen as a proaromatic electron acceptor.

The target merocyanines incorporating an acyclic spacer (**3**, **5a**, and **5b**) were prepared by reaction of **1** with

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(1) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, 1997.

(2) Wolf, J. J.; Wortmann, R. *Adv. Phys. Org. Chem.* **1999**, *32*, 121.

(3) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103.

(4) (a) Marder, S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science* **1994**, *263*, 511. (b) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845.

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(6) Ikeda, H.; Sakai, T.; Kawasaki, K. *Chem. Phys. Lett.* **1991**, *179*, 551. The $\mu\beta_0$ values reported in this work do not make it possible to ascertain the effect of lengthening the π spacer on the NLO properties of the NLO-phores reported therein.

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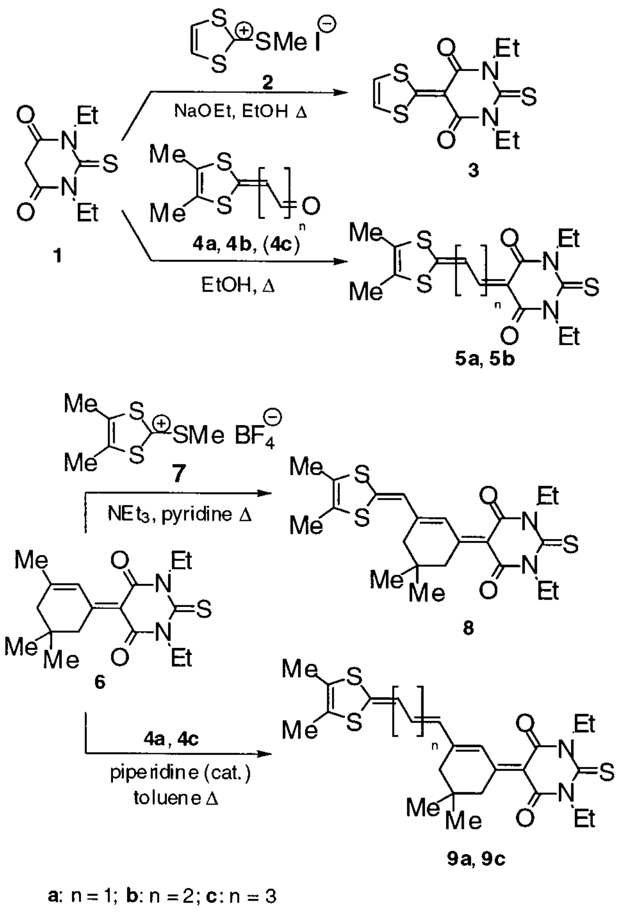
dithiolium salt **2** or aldehydes **4a** and **4b**, respectively (Scheme 1).

Scheme 1



Unfortunately, all attempts to isolate the higher vinylogue **5c**, from the reaction of **1** with **4c**, failed as a result of extensive decomposition in a variety of solvents, even in the absence of light. Since the instability of some push–pull polyenes is a well-known issue, we reasoned that incorporation of a partially rigidified spacer could increase the stability of the desired NLO-phores. In fact, reaction of compound **6** with **4a** and **4c** afforded **9a** and **9c**, with four and six double bonds in the spacer, respectively. Moreover, compound **8**, directly analogous to **5b**, was prepared (by reaction of **6** with salt **7**) with a view to study the effect of the introduction of the cyclohexene moiety on the linear and nonlinear optical properties of these NLO-phores.

Relevant electrochemical and optical characterization data are gathered in Table 1. Cyclovoltammetric data indicate that oxidation of the dithiafulvene moiety and reduction of the thiobarbituric unit (both chemically irreversible processes) become increasingly easier on lengthening the π-spacer, indicating a smaller contribution of the charge-separated form to the ground state of the longer derivatives.

The electronic absorption spectra of these merocyanines display a broad, low-energy intramolecular charge transfer band and show a bathochromic shift on increasing the length of the spacer, although the introduction of the isophorone-derived moiety results not only in a hypsochromic effect (cf. **5b** and **8**) but also in a leveling off of the λ_{max} values. Moreover, all of these compounds show a positive solvatochromism (λ_{max} values in DMSO: **3**, 405 nm; **5a**, 564 nm; **5b**, 655 nm; **8**, 646 nm; **9a**, 661 nm; **9c**, 644 nm), although the solvatochromic shift of **3** is very small.

Table 1. Redox Potentials (V), Absorption Spectra (nm), and $\mu\beta$ (10^{-48} esu) for CH_2Cl_2 Solutions

compound	E_{ox}[a]	E_{red}[a]	λ_{max} (log ϵ)	$\mu\beta$[b]	$\mu\beta_0$[c]
3	1.55	−1.48	403 (4.81)	−12	−9
5a	1.16	−1.00	558 (5.05)	100	60
5b	0.87	−0.85	642 (5.00)	1100	525
8	0.81	−0.96	630 (4.67)	440	221
9a	0.65	−0.81	638 (4.50)	2315	1135
9c	0.48	−0.77	638 (3.87)	2746	1350

[a] Versus Ag/AgCl, glassy carbon working electrode, 0.1 M TBAPF$_6$, 0.1 V s^{-1}. [b] Measured at 1907 nm. [c] Calculated using the two-level model.

The second-order NLO properties of the NLO-phores were determined by EFISH. The measured $\mu\beta_0$ values, determined using the two-level model, range from -9×10^{-48} esu for **3** to 1350×10^{-48} esu for **9c**. Inspection of Table 1 reveals that, for the same type of spacer, $\mu\beta_0$ values increase with the conjugation path, and that introduction of the isophorone-derived bridge gives rise to a decrease of $\mu\beta_0$ when compared to an acyclic spacer of the same conjugation length (**5b** and **8**). It should be noted that $\mu\beta_0$ for **9c** is about four times larger than for DANS (4-(dimethylamino)-4′-nitrostilbene), a common benchmark for second-order NLO-phores. Moreover, compound **3** is the only one to show a small but negative value.

Ab initio and DFT calculations have been carried out on model compounds **10** (Figure 1) in order to disclose the role of the proaromaticity of the end groups on the properties of these NLO-phores.

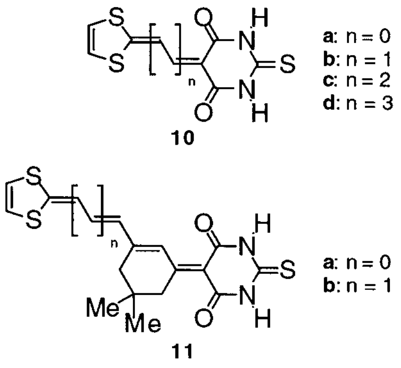


Figure 1. Model compounds theoretically studied.

Since bond length alternation (BLA) is a crucial parameter in the design of optimized NLO-phores,[4] BLA values were calculated using B3P86/6-31G* geometries, which are in very good agreement with crystal structures for 1,3-dithiole derivatives.[10] The most relevant results of the calculations are gathered in Table 2.

Table 2. Calculated BLA (Å), Charge on the Dithiole Ring (e), and $\mu\beta_0$ (10^{-48} esu) for Model Compounds **10**

compound	BLA^a	charge^b	$\mu\beta_0$ (calc)^b
10a		+0.344	−62
10b	−0.029	+0.207	2
10c	−0.040	+0.129	437
10d	−0.043	+0.086	1363

^{a} B3P86/6-31G*. ^{b} HF/6-31G*//B3P86/6-31G*.

It can be seen that lengthening the π-spacer results in an increase of |BLA| together with a decrease of the charge on the dithiole ring. This implies that the gain in aromaticity at the end groups and the contribution of the zwitterionic limiting form to the ground state of these molecules are more important for the shorter derivatives. This is confirmed by the small negative $\mu\beta_0$ value displayed by compound **3**, implying that $\mu_g > \mu_e$ (where g and e refer to the ground and excited states, respectively). Its very weak solvatochromism also suggests that this molecule is close to the cyanine limit and, therefore, lies in region C, according to Marder's classification.[11]

Compound **10b** shows a reduced BLA, which is confirmed by the ^{1}H NMR spectrum of **5a** in $CDCl_3$. The large value of $^3J_{HH}$ (13.80 Hz) across the central bond of the spacer suggests a substantial character of *trans* double bond and a noticeable contribution of the zwitterionic form. On the other hand, BLA for the longer derivatives **10c** and **10d** (ca. −0.04 Å) lie in the optimum range (|0.05 ± 0.01|) for obtaining high β values, in good agreement with the calculated and observed trends. These NLO-phores have more polyene-like electronic structures, which nevertheless can be modified by the surrounding medium; thus, in a more polar environment an increase in the contribution of the charge-separated form to the ground state is to be expected. This is confirmed by the calculated BLA for **10c** in DMSO (−0.020 Å) and by EFISH measurements of **9a** in DMSO ($\lambda_{max} = 661$ nm, $\mu\beta_0 = 658 \times 10^{-48}$ esu; cf. Table 1); this decrease in $\mu\beta_0$ stems from solvent stabilization of the zwitterionic limiting form, with a concomitant decrease of $\mu_e - \mu_g$. Therefore, these derivatives lie in the so-called region B.[11]

Although CPHF calculations correctly reproduce the observed trend in the $\mu\beta_0$ values of these NLO-phores, a more intuitive picture of their NLO properties comes from the two-level model. In this simplified treatment $\beta \propto \Delta\mu \cdot f_{ge}/E^3$, where $\Delta\mu = \mu_e - \mu_g$, and f_{ge} and E are the oscillator strength and the energy of the intramolecular charge-transfer transition, respectively. On passing from **10a** to **10d**, TD-DFT calculations show an increase in f_{ge} and a decrease in E but, more important, predict a smooth increase in μ_g and a steeper increase in μ_e. Therefore, $\Delta\mu$ rapidly increases along this series and, being negative for **10a**, an inversion in the sign of $\Delta\mu$ is calculated to occur near **10b** (Figure 2).

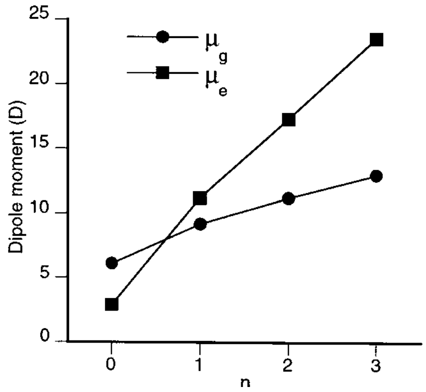


Figure 2. Calculated μ_e and μ_g values for compounds **10**.

This explains the low $\mu\beta$ values calculated for some dithiole-π-acceptor NLO-phores incorporating two C=C bonds ($n = 1$) in the spacer, a fact that has been erroneously attributed by some authors to a poor electron-donating ability (or even an electron-withdrawing character) of the 1,3-dithiole unit.[12]

Theoretical calculations on model compound **11a** (Figure 1) also account for the observed hypsochromic effect[13] and the marked decrease of $\mu\beta$ on passing from **5b** to **8**. Thus, bond angle deviations from 120° along the spacer, together with a slight distortion from planarity, give rise to a blue-shifted transition for the isophorone NLO-phores.

Moreover, the angle between μ and β vectors for **11a** (51.8°) is much larger than for its open-chain analogue **10c** (21.1°), resulting in a smaller calculated $\mu\beta_0$ value for the former (248×10^{-48} esu, in excellent agreement with that measured for compound **8**). The detrimental effect of the cyclic spacer on the NLO properties of these compounds is confirmed by the calculated $\mu\beta_0$ value of **11b** (972×10^{-48} esu) which is notably lower than that calculated for its acyclic analogue with four C=C double bonds in the spacer, **10d** (cf. Table 2).

Because the second-order NLO properties of linear tetrathiafulvalene (TTF)-related NLO-phores (such as **12**) have been reported,[14] we have synthesized compound **13**[15]

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(Figure 3) in order to ascertain the effect of the isophorone moiety on the optical properties of this series and to compare the relative efficiency of the dithiole and the TTF groups as donors.

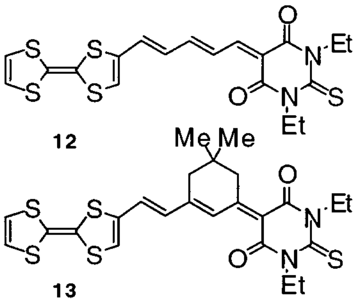

Figure 3. Related TTF-Containing NLO-phores.

In this case, the hypsochromic effect due to the presence of the cyclohexene ring is very large (λ_{max} = 555 nm for **13**, 648 nm for **12**, both in CH_2Cl_2) and the $\mu\beta_0$ values also decrease on incorporation of the cyclic spacer (**13** $\mu\beta_0 = 375 \times 10^{-48}$ esu (CH_2Cl_2); **12** $\mu\beta_0 = 455 \times 10^{-48}$ esu (DMSO)).

A comparison of the optical properties of the 1,3-dithiole NLO-phores herein reported with those of the TTF-thiobarbituric series[14] reveals that (a) lengthening the π spacer in the former series results in a bathochromic shift, in sharp contrast to the unusual hypsochromic shift observed with the TTF derivatives,[14] and (b) the 4,5-dimethyl-1,3-dithiole unit is a more efficient donor than the TTF moiety for a given number of conjugated atoms. This can be related to the larger HOMO coefficient at the exocyclic atom of the dithiafulvene fragment, when compared to the HOMO coefficient at the outer carbon atoms of TTF, and to the gain in aromaticity of the ditiole on charge-transfer excitation. Moreover, the second-order NLO response of compounds **5**, **8**, and **9** indicates that the efficiency of the 4,5-dimethyl-1,3-dithiole unit is similar to that of trimethylindoline or some di-iron ethylidene complexes reported.[16]

To sum up, the proaromatic character of the 1,3-dithiole group gives rise to high $\mu\beta$ values, provided long spacers are used; lengthening the polyenic chain results in large photoinduced changes in the dipole moment and enhanced hyperpolarizabilities. The negative $\mu\beta$ value for the shortest derivative demonstrates the importance of the zwitterionic form in the description of its ground state. Experimental and theoretical results demonstrate that the 1,3-dithiole moiety, far from displaying an electron-withdrawing character, is a more efficient π electron-donor than TTF in dipolar D-π-A NLO-phores.

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Supporting Information Available: Experimental procedures and spectroscopic characterization of new compounds and description of the experimental setup for EFISH measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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