Tetrahedron Letters 51 (2010) 6863–6866

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# Benzothiazolium-π-thiazole-dicyanomethanides: new nonlinear optical chromophores

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## ARTICLE INFO

*Article history:*
Received 17 September 2010
Revised 18 October 2010
Accepted 20 October 2010
Available online 26 October 2010

Dedicated to the memory of Professor Michel Jubault, good friend and warm-hearted colleague

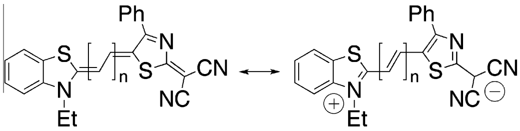
*Keywords:*
Benzothiazole
Thiazole
Nonlinear optics

## ABSTRACT

A series of merocyanines with a benzothiazolylidene donor and a quinoidal thiazole moiety have been synthesized. Experimental results and theoretical calculations show that these compounds have zwitterionic ground states and negative second-order optical nonlinearities. Unlike most merocyanines, the degree of charge transfer does not decrease on increasing the separation between the donor and the acceptor groups, an unexpected feature related to the presence of the proaromatic thiazole fragment.

Benzothiazole-containing cyanines and merocyanines display interesting optical properties and have found numerous applications,[1] such as sensitizing dyes in photography, photosensitizers in medicine, fluorescent labels for bioimaging and dyes for dye-sensitized solar cells,[2] to name just a few. In the field of second-order nonlinear optics (NLO),[3] where push-pull compounds with an electron donor (D) and an electron acceptor (A) linked through a conjugated spacer have been extensively studied, benzothiazoles have also demonstrated their versatility. Thus, they can play the role of acceptors,[4] spacers[5] and even donors when 2-benzothiazolylidene fragments are conjugated to acceptor groups. In that case, the gain in aromaticity of the hetarylidene moiety (its 'proaromatic' character) upon charge-transfer (CT) increases the zwitterionic (benzothiazolium-like) character of these derivatives and lies behind their second-order NLO responses. A variety of acceptors have been used to that end,[6] but the linking of an additional proaromatic fragment to the benzothiazolylidene group as a strategy towards efficient NLO-chromophores has been little studied, and mainly in connection with proaromatic acceptors.[7] On the other hand, there are very few reports in the literature on merocyanines comprising of a benzothiazolylidene donor and a proaromatic spacer,[8] and in such compounds the latter fragment is carbocyclic. To the best of our knowledge there are no examples of related structures bearing a heterocyclic proaromatic spacer and, given the growing interest in thiazoles as spacers (and auxiliary acceptors) for NLO-chromophores,[9] in this Letter we report the synthesis, characterization and linear and nonlinear optical properties of merocyanines **1**, endowed with two proaromatic fragments, a benzothiazolylidene donor and a thiazole-2,5-diylidene moiety (Fig. 1). According to our expectations, and because of the increased aromaticity on charge separation, these compounds turn out to be zwitterionic, highly efficient second-order NLO chromophores.

Compounds **1a–c** were synthesized as shown in Scheme 1. Thus, **1a** was prepared by the reaction of 2-dicyanomethylene-2,3-dihydro-4-phenylthiazole (**2**)[10] and 2-(2-acetanilidovinyl)-3-ethylbenzothiazolium iodide (**3**)[11] in the presence of triethylamine. A complementary strategy, using a nucleophilic benzothiazole reagent, was adopted for the synthesis of the longer derivatives (**1b,c**). Thus, the new acceptors **5b,c**, in turn prepared from **2** and the corresponding dianilide hydrochlorides (**4b** and **4c**,



**1a**: n = 1; **1b**: n = 2; **1c**: n = 3

**Figure 1.** Merocyanines **1a–c** prepared.

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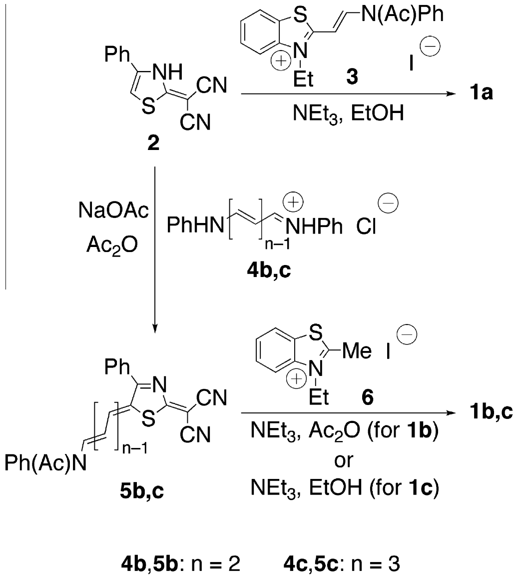
doi:10.1016/j.tetlet.2010.10.103

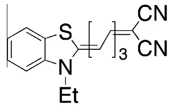


**Scheme 1.** Synthesis of compounds **1a–c**.

respectively), were made to react with 3-ethyl-2-methylenebenzothiazole, in situ generated from the commercially available benzothiazolium salt **6** and $NEt_3$.

Concerning the stereochemistry of compounds **1**, $^3J_{HH}$ coupling constant analysis indicates an all-*trans* geometry along the polyenic chain, whereas the benzothiazole-exocyclic C=C bond is assumed to have (*Z*)-geometry, in keeping with previous crystallographic studies on benzothiazolylidene-derived merocyanines.[8b,12]

Moreover, $^3J_{HH}$ values along the polyenic spacer afford valuable information concerning the ground state polarization of these compounds, given the existing correlation between $^3J_{HH}$ values and C–C bond lengths.[13] Thus, the high $^3J_{HH}$ value (14.2 Hz in DMSO-$d_6$) for the protons of the dimethine spacer of **1a** points to a noticeable double bond character for the formally single =HC–CH= bond and, therefore, to an important zwitterionic contribution to the ground state of this compound. (As expected, such contribution slightly decreases in the less polar solvent acetone-$d_6$, as judged from the corresponding $^3J_{HH}$ value of 13.9 Hz). For the longer derivatives, the $\Delta J$ values (defined as the difference between the averaged $^3J_{HH}$ values of the formal double and single C–C bonds along the polymethine chain)[14] provide a clear indication of the ground state polarization. Taking into account that for all-*trans* polyenes $\Delta J \approx 6$ Hz and for cyanines $\Delta J \approx 0$ Hz,[15] the $\Delta J$ values measured for **1b** (−3.1 Hz) and **1c** (−2.8 Hz) in DMSO-$d_6$ turn out to be relatively small and negative, indicating that the ground states of these compounds also lie between the ideal polymethine state (cyanine limit) and the fully zwitterionic limiting form. In agreement with the strong polarization of these merocyanines, the chemical shifts of their polymethine protons show an oscillatory behaviour[16] that reflects the alternation in the electron densities of the carbon atoms to which they are bonded (e.g., for **1b** in DMSO-$d_6$ such $\delta_H$ values, starting from the benzothiazole end group, are: 7.28, 8.08, 6.63 and 7.64 ppm, respectively). In order to analyse the role that the quinoidal thiazole unit plays in these chromophores it is instructive to compare the properties of **1a** and its polyenic analogue **7** of the same conjugation length[17] (Fig. 2). Thus, whereas the latter is close to the cyanine limit, as evidenced by the nearly identical $^3J_{HH}$ values along the polymethine chain (12.5–12.6 Hz in DMSO-$d_6$), the corresponding $^3J_{HH}$ value for the dimethine spacer of **1a** is considerably higher (14.2 Hz). This fact, together with the deshielding of the $NCH_2$ group on passing from **7** (4.17 ppm) to **1a** (4.72 ppm), show that the introduction of the quinoidal thiazole fragment in the spacer gives rise to merocyanines with an enhanced zwitterionic character.



**7**

**Figure 2.** Structure of model compound **7**.

Theoretical calculations have been carried out using the polarized continuum model (PCM) in DMSO, in order to correlate with experimental measurements, and provide a useful insight into the structure and properties of compounds **1**. Thus, inspection of Table 1 shows that these compounds have very low and negative bond length alternation (BLA) values,[18] as determined from the calculated bond lengths along the polyenic spacer (Fig. 3), suggesting a predominant contribution of the zwitterionic limiting form to the description of their ground states, in agreement with the previously discussed $^1H$ NMR data.

This feature is confirmed by the high Mulliken charges on the donor and acceptor (dicyanomethylene) end groups and by the negative values of the variation of the donor charge on excitation, $\Delta q$(D), which suggest a decreased zwitterionic character of their first excited states.

Moreover, inspection of the bond lengths of the heterocyclic moieties on lengthening the spacer reveals an intriguing feature. Thus, the slight decrease in the length of benzothiazole bond *a* (Fig. 3) on passing from **1c** to **1a**, together with the concomitant increase in bond length *b*, reveals that the cationic character of the benzothiazole moiety decreases in the series **1a** > **1b** > **1c** (as it usually happens in merocyanines, given the growing difficulty in separating opposite charges over larger distances).[19] On the other hand, the bond lengths of the thiazole rings and of the thiazole–$C(CN)_2$ bonds show that the anionic character of the dicyanomethylenethiazole fragment increases from **1a** to **1c**. Moreover, these two opposite trends are in good agreement with the results of Mulliken calculations (Table 1). This seeming contradiction can be solved taking into account the small electron donor effect of the spacer, which increases for the longer derivatives, as revealed by the corresponding Mulliken spacer charges (**1a**: +0.03; **1b**: +0.07; **1c**: +0.09).

IR spectroscopy provides an experimental evidence supporting the nondecreasing amount of charge transfer on lengthening the spacer. It is known that the $\nu(C\equiv N)$ band is very sensitive to the electron density on the nitrile groups, downshifting upon CT in the case of push–pull compounds bearing a dicyanomethylene acceptor.[20] The C≡N stretching modes of compounds **1**, measured by attenuated total reflectance (**1a**: 2191, 2162 $cm^{-1}$; **1b**: 2181, 2154 $cm^{-1}$; **1c**: 2183, 2148 $cm^{-1}$), show not only the characteristic low frequencies and splittings expected for the acceptor bearing an excess of electron density,[21] but also a noticeable downshift of the $\nu(C\equiv N)$ vibrations on passing from **1a** to **1b,c**. This reveals a larger

**Table 1**
Selected calculated[a] bond lengths, BLA and Mulliken charges

| Compound | *a*[b] | *b*[b] | BLA[b] | *q*(D)[c] | *q*(A)[d] | $\Delta q$(D)[e] |
|---|---|---|---|---|---|---|
| **1a** | 1.354 | 1.402 | −0.016 | +0.54 | −0.57 | −0.06 |
| **1b** | 1.355 | 1.401 | −0.014 | +0.52 | −0.59 | −0.05 |
| **1c** | 1.356 | 1.399 | −0.014 | +0.51 | −0.60 | −0.05 |

[a] Calculated at the PCM-B3P86/6-31G*//B3P86/6-31G* level in DMSO.
[b] In Å, see Figure 3.
[c] Charge on the donor (ethylbenzothiazole fragment).
[d] Charge on the acceptor (dicyanomethylene fragment).
[e] Variation of the charge on the donor upon excitation.

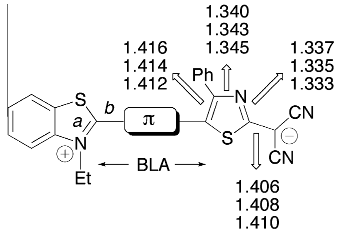


**Figure 3.** Selected bond lengths (from top to bottom: **1a** to **1c**) and structural parameters.

**Table 2**
Electrochemical and optical properties and calculated $E_{HOMO}/E_{LUMO}$ values

| Compound | $E_{ox}$[a] | $E_{red}$[a] | $E_{HOMO}$[b] | $E_{LUMO}$[b] | $\lambda_{max}$ (log $\varepsilon$)[c] | $\lambda_{max}$[d] |
|---|---|---|---|---|---|---|
| **1a** | +0.85 | −0.92 | −5.98 | −3.51 | 592 (sh), 636 (5.08) | 608 |
| **1b** | +0.64 | −0.78 | −5.79 | −3.61 | 674 (sh), 739 (5.09) | 669 |
| **1c** | +0.60 | −0.67 | −5.65 | −3.70 | 850[e] | 681 |

[a] $E$ in V versus Ag/AgCl, glassy carbon working electrode, $TBAPF_6$ 0.1 M in $CH_2Cl_2$, 0.1 V/s. Ferrocene internal reference $E_{ox}$ = +0.51 V.
[b] In eV. Calculated at the PCM-B3P86/6-31G*//B3P86/6-31G* level in DMSO.
[c] In nm, measured in $CH_2Cl_2$.
[d] In nm, measured in DMSO.
[e] log $\varepsilon$ not determined due to its very low solubility.

zwitterionic contribution for the longer derivatives, in line with the results of theoretical calculations.

The redox properties of the target compounds were measured by cyclic voltammetry (Table 2). Compounds **1a–c** show two irreversible waves, corresponding to the oxidation of the donor and the reduction of the acceptor, respectively, and it can be seen that the oxidation and the reduction processes become easier on chain lengthening, in agreement with the trends shown by the calculated HOMO and LUMO energies. This behaviour can be related to the stability of the electrochemically generated ion-radicals, which are more effectively delocalized in the longer derivatives due to the increased extension of the π system.

The UV–vis absorption data of chromophores **1**, studied in dichloromethane and DMSO, are collected in Table 2. All compounds show strong absorption bands in the visible region, extending into the near-infrared for the longest derivative **1c**. It can be seen that in dichloromethane, lengthening the spacer gives rise to large vinylene shifts, even exceeding the typical value for cyanines (ca. 100 nm), whereas in DMSO such shifts are much lower (**1a** to **1b**: 61 nm, **1b** to **1c**: 12 nm). These trends reveal that compounds **1** are close to the ideal polymethine state in dichloromethane and that the increase in solvent polarity gives rise to more localized structures, in agreement with $^1$H NMR data. Moreover, the negative solvatochromism shown by **1a–c** points to a decrease in their dipole moments upon excitation and, therefore, to zwitterionic ground states. The observed band broadening in DMSO is indicative of stronger polar interactions in this solvent, as confirmed by the increase in the negative solvatochromism on lengthening the spacer (28 nm (724 $cm^{-1}$) for **1a**; 70 nm (1416 $cm^{-1}$) for **1b**; 169 nm (2920 $cm^{-1}$) for **1c**). Besides, a comparison of the UV–vis data of **7** (slightly positive solvatochromism and decreased bandwidth on increasing solvent polarity)[17] and **1a** confirms that the replacement of one C═C bond in the spacer by a quinoidal thiazole results in merocyanines with an increased charge separation. This observation suggests that the thiazole ring is not only a π-conjugated spacer, but also an auxiliary acceptor group.

The second-order NLO figures of merit, $\mu\beta$, (where $\beta$ is the first molecular hyperpolarizability) of **1a–c** were measured by electric field-induced second harmonic generation (EFISH) at 1907 nm in DMSO (Table 3), and the $\mu\beta_0$ values (extrapolated at zero frequency) were calculated by the two-level model,[22] using the lowest energy absorption band of each compound. EFISH measurements in dichloromethane were undertaken as well and the experimental results pointed to negative nonlinearities, although the poor solubility in this solvent precluded us to obtain reliable $\mu\beta$ values. (For the sake of comparison, Disperse Red 1 in dichloromethane gives a $\mu\beta_0$ value of 480 × $10^{-48}$ esu under the same experimental conditions).

**Table 3**
Experimental and calculated optical nonlinearities[a] and TDDFT-calculated parameters

| Compound | Exp (DMSO) | | CPHF[b] | | TDDFT[c] | | |
|---|---|---|---|---|---|---|---|
| | $\mu\beta$[d] | $\mu\beta_0$[e] | $\mu$[f] | $\mu\beta_0$ | $E$[g] | $f$ | $\Delta\mu_{ge}(z)$[f] |
| **1a** | −820 | −440 | 30.85 | −5533 | 2.09 | 1.47 | −3.19 |
| **1b** | −4300 | −1900 | 37.94 | −16304 | 1.83 | 1.96 | −3.58 |
| **1c** | −5300 | −2300 | 45.45 | −45921 | 1.63 | 2.45 | −4.56 |

[a] $\mu\beta$ and $\mu\beta_0$ values in $10^{-48}$ esu.
[b] Calculated at the PCM-CPHF/6-31G*//6-31G* level in DMSO.
[c] Calculated at the PCM-B3P86/6-31G*//B3P86/6-31G* level in DMSO.
[d] Measured at 1907 nm. Experimental accuracy: ±10%.
[e] Determined using the two-level model.
[f] In Debyes.
[g] In eV.

It can be seen that compounds **1** show increasingly negative $\mu\beta$ values on lengthening the spacer. This trend is reproduced by Coupled-perturbed Hartree-Fock (CPHF) calculations, although the inclusion of the solvent gives rise to largely overestimated NLO responses. In order to get a better understanding of the nonlinear optical properties of **1a–c**, TDDFT calculations have also been carried out, since they provide the parameters involved in the two-level model: in this approach $\beta_0 \propto \Delta\mu_{ge} f/E^3$, where $\Delta\mu_{ge}$ is the difference between the excited- and ground-state dipole moments ($\mu_e$ and $\mu_g$, respectively), $f$ is the oscillator strength and $E$ is the first excitation energy. These parameters are also gathered in Table 3 although, to provide a clearer picture of the CT direction on excitation, $\Delta\mu_{ge}$ has been replaced by $\Delta\mu_{ge}(z)$, defined as the projection of $\Delta\mu_{ge}$ onto the ground state dipole moment direction. It can be seen that the negative $\Delta\mu_{ge}(z)$ values lie behind the negative NLO responses and that the decrease in $E$, together with the calculated increases in $f$ and in $|\Delta\mu_{ge}|$ are responsible for the observed increase in $\mu\beta_0$ values on passing from **1a** to **1c**. Therefore, compounds **1** can be classed as 'right-hand side' NLO-chromophores.[23] Unfortunately, their limited solubility has precluded a comparative study of their second-order NLO responses in different solvents and, therefore, a more precise placement of such compounds in either region D or E of Marder's plot.

In summary, benzothiazolium-thiazole-dicyanomethanides **1**, comprising of a formal benzothiazolylidene donor and a quinoidal thiazole fragment, presumably acting as spacer and auxiliary acceptor, have been prepared for the first time and shown to display negative second-order optical nonlinearities. The gain in aromaticity experienced by the two heterocyclic moieties upon charge transfer results in merocyanines with a strong zwitterionic character that, surprisingly enough, does not decrease on lengthening the spacer. The increased charge separation due to the presence of the quinoidal thiazole fragment, ascertained by comparison with a polyenic analogue, can be relevant in the design of new zwitterionic NLO-chromophores.

## Acknowledgements

We thank Dr. J. Casado (Universidad de Málaga) for the ATR-IR spectra. Financial support from MICINN-FEDER (CTQ2008-02942 and MAT2008-06522C02-02) and Gobierno de Aragón-Fondo Social Europeo (E39) is gratefully acknowledged. Predoctoral fellowships to E.G. (CSIC, JAE 2008) and R. Alicante (FPI BES 2006-12104) are also acknowledged.

## Supplementary data

Supplementary data (general experimental methods, synthesis and characterization of new compounds, UV–vis spectra, NLO measurements and computational procedures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.103.

## References and notes

1. (a) Hamer, F. M. *The Cyanine Dyes and Related Compounds*; Wiley-Interscience: New York, 1964; (b) Larivé, H.; Dennilauler, R. In *Thiazole and its Derivatives*; Metzger, J. V., Ed.; Wiley-Interscience: New York, 1979; pp 23–216. Part 3; (c)*Functional Dyes*; Kim, S.-H., Ed.; Elsevier: Amsterdam, 2006; (d)*Heterocyclic Polymethine Dyes: Synthesis, Properties and Applications*; Strekowski, L., Ed.; Springer: Berlin, 2008.
2. Sayama, K.; Tsukagoshi, S.; Mori, T.; Hara, K.; Ohga, Y.; Shinpou, A.; Abe, Y.; Suga, S.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2003**, *80*, 47–71.
3. (a) Cho, M. J.; Choi, D. H.; Sullivan, P. A.; Akelaitis, A. J. P.; Dalton, L. R. *Prog. Polym. Sci.* **2008**, *33*, 1013–1058; (b) Luo, J.; Zhou, X.-H.; Jen, A. K.-Y. *J. Mater. Chem.* **2009**, *19*, 7410–7424; (c) Dalton, L. R.; Sullivan, P. A.; Bale, D. H. *Chem. Rev.* **2010**, *110*, 25–55.
4. (a) Coe, B. J.; Harris, J. A.; Hall, J. J.; Brunschwig, B. S.; Hung, S.-T.; Libaers, W.; Clays, K.; Coles, S. J.; Horton, P. N.; Light, M. E.; Hursthouse, M. B.; Garín, J.; Orduna, J. *Chem. Mater.* **2006**, *18*, 5907–5918; (b) Costa, S. P. G.; Batista, R. M. F.; Cardoso, P.; Belsley, M.; Raposo, M. M. M. *Eur. J. Org. Chem.* **2006**, 3938–3946; (c) Batista, R. M. F.; Costa, S. P. G.; Malheiro, E. L.; Belsley, M.; Raposo, M. M. M. *Tetrahedron* **2007**, *63*, 4258–4265; (d) Zajac, M.; Hrobárik, P.; Magdolen, P.; Foltínová, P.; Zahradník, P. *Tetrahedron* **2008**, *64*, 10605–10618.
5. (a) Hrobarik, P.; Zahradnik, P.; Fabian, W. M. F. *Phys. Chem. Chem. Phys.* **2004**, *6*, 495–502; (b) Benková, Z.; Černušák, I.; Zahradník, P. *Struct. Chem.* **2006**, *17*, 287–300.
6. (a) Kay, A. J.; Woolhouse, A. D.; Zhao, Y.; Clays, K. *J. Mater. Chem.* **2004**, *14*, 1321–1330; (b) Latorre, S.; Moreira, I. deP. R.; Villacampa, B.; Julià, L.; Velasco, D.; Bofill, J. M.; López-Calahorra, F. *ChemPhysChem* **2010**, *11*, 912–919.
7. (a) Ikeda, H.; Sakai, T.; Kawasaki, K. *Chem. Phys. Lett.* **1991**, *179*, 551–554; (b) Cho, B. R.; Je, J. T.; Lee, S. J.; Lee, S. H.; Kim, H. S.; Jeon, S. J.; Song, O.-K.; Wang, C. H. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2141–2144; (c) Kay, A. J.; Woolhouse, A. D.; Gainsford, G. J.; Haskell, T. G.; Barnes, T. H.; McKinnie, I. T.; Wyss, C. P. *J. Mater. Chem.* **2001**, *11*, 996–1002.
8. (a) Ashwell, G. J.; Malhotra, M.; Bryce, M. R.; Grainger, A. M. *Synth. Met.* **1991**, *43*, 3173–3176; (b) Bell, N. A.; Crouch, D. J.; Simmonds, D. J.; Goeta, A. E.; Gelbrich, T.; Hursthouse, M. B. *J. Mater. Chem.* **2002**, *12*, 1274–1279.
9. (a) Breitung, E. M.; Shu, C.-F.; McMahon, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1154–1160; (b) Schmidt, K.; Leclercq, A.; Zojer, E.; Lawson, P. V.; Jang, S.-H.; Barlow, S.; Jen, A. K.-Y.; Marder, S. R.; Brédas, J.-L. *Adv. Funct. Mater.* **2008**, *18*, 794–801; (c) Ma, X.; Ma, F.; Zhao, Z.; Song, N.; Zhang, J. *J. Mater. Chem.* **2010**, *20*, 2369–2380.
10. Seybold, G. U.S. Patent 4,371,734, 1983; *Chem. Abstr.* **1983**, *98*, 198202.
11. Brooker, L. G. S.; White, F. L.; Keyes, G. H.; Smyth, C. P.; Oesper, P. F. *J. Am. Chem. Soc.* **1941**, *63*, 3192–3203.
12. Nüesch, F.; Grätzel, M.; Nesper, R.; Shklover, V. *Acta Crystallogr., Sect. B* **1996**, *52*, 277–286.
13. Radeglia, R.; Dähne, S. *J. Mol. Struct.* **1970**, *5*, 399–411.
14. Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science* **1993**, *261*, 186–189.
15. Scheibe, G.; Seiffert, W.; Hohlneicher, G.; Jutz, Ch.; Springer, H. J. *Tetrahedron Lett.* **1966**, *7*, 5053–5059.
16. Kulinich, A. V.; Ishchenko, A. A.; Groth, U. M. *Spectrochim. Acta, Part A* **2007**, *68*, 6–14.
17. Kulinich, A. V.; Derevyanko, N. A.; Ishchenko, A. A. *Russ. Chem. Bull.* **2005**, *54*, 2820–2830.
18. Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Gorman, C. B.; Gilmour, S.; Biddle, S. L.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, *115*, 2524–2526.
19. (a) Alías, S.; Andreu, R.; Blesa, M. J.; Franco, S.; Garín, J.; Gragera, A.; Orduna, J.; Romero, P.; Villacampa, B.; Allain, M. *J. Org. Chem.* **2007**, *72*, 6440–6446; (b) Andreu, R.; Carrasquer, L.; Franco, S.; Garín, J.; Orduna, J.; Martínez de Baroja, N.; Alicante, R.; Villacampa, B.; Allain, M. *J. Org. Chem.* **2009**, *74*, 6647–6657.
20. Casado, J.; Moreno Oliva, M.; Ruiz Delgado, M. C.; López Navarrete, J. T.; Sánchez, L.; Martín, N.; Andreu, R.; Carrasquer, L.; Garín, J.; Orduna, J. *J. Chem. Phys.* **2007**, *126*, 074701-1–074701-8.
21. Binev, Y. I.; Georgieva, M. K.; Novkova, S. I. *Spectrochim. Acta, Part A* **2003**, *59*, 3041–3052.
22. Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664–2668.
23. Bourhill, G.; Brédas, J.-L.; Cheng, L.-T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc.* **1994**, *116*, 2619–2620.