Pergamon

Tetrahedron Letters 39 (1998) 3577–3580

TETRAHEDRON
LETTERS

Second-order nonlinear optical properties of tetrathiafulvalene-π-(thio)barbituric acid chromophores

Javier Garín,*[a] Jesús Orduna,[a] José Ignacio Rupérez,[a] Rafael Alcalá,[b] Belén Villacampa,[b] Carlos Sánchez,[b] Nazario Martín,[c] José Luis Segura [c] and Mar González [c]

[a] *Departamento de Química Orgánica, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza (Spain)*
[b] *Departamento de Física de la Materia Condensada, ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza (Spain)*
[c] *Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense de Madrid, E-28040 Madrid (Spain)*

Received 10 February 1998; accepted 6 March 1998

Abstract

Donor-acceptor polyenes that combine an electron-donating tetrathiafulvalene (TTF) unit with a barbituric or thiobarbituric acid have been prepared for the first time and characterized as nonlinear optical (NLO) chromophores. The electrochemical and thermal properties of these derivatives are also reported.

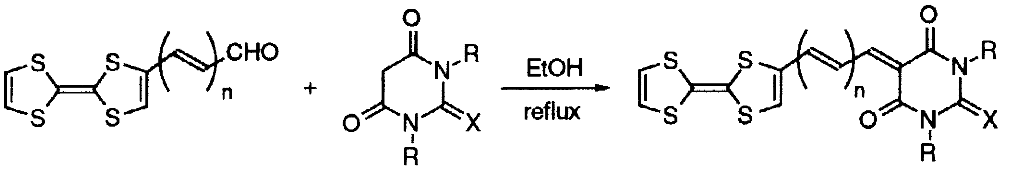
Keywords: Thiafulvalenes; electronic spectra; electrochemistry; theoretical studies.

Push-pull systems of general structure D-π-A (where D is an electron-donating group, π is a π-conjugated system and A is an electron-withdrawing group) are being actively studied as nonlinear optical chromophores [1], since they can exhibit large quadratic molecular hyperpolarizabilities (β). Thus, a great deal of effort has been devoted to the design of efficient NLO chromophores, incorporating new donors, acceptors and conjugated spacers [2-4]. Given the importance of the gain in aromaticity in the zwitterionic limiting form of these systems, it is not surprising that barbituric acid and its derivatives have been widely used as powerful acceptor groups [5-9]. On the other hand, many different donor groups have also been studied, such as anilines, thiophenes, ferrocenes and 1,4-dithiafulvenes [10,11], all of which are of clear interest in the fields of electroactive and/or conducting materials. Nevertheless, the effect of a tetrathiafulvalene group on the second-order NLO properties of push-pull polyenes has been much less studied. We recently reported the first results in this area, using moderately electron-acceptor groups, such as formyl and dicyanomethylene [12,13], and in this paper we report the synthesis, nonlinear optical, redox and thermal properties of the first TTF-π-(thio)barbituric acid derivatives.

Compounds **5a-c**, **6a-c** and **7c** were prepared by Knoevenagel reactions of aldehydes **1**, **2** [14] and **3** [15] with barbituric acid derivatives **4** (Scheme). Best results (**5a-c**: 32-60%, **6a-c**: 62-82%, **7c**: 55%) were obtained by simply refluxing stoichiometric amounts of both reagents in ethanol, while the mixture was protected from light and oxygen. The attempted

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00553-X

use of different catalysts, such as ethylenediammonium diacetate or piperidine [5] invariably led to decomposition products.



1 n = 0
2 n = 1
3 n = 2

4a-c

5a-c n = 0
6a-c n = 1
7c n = 2

a: R = H, X = O; **b**: R = Me, X = O; **c**: R = Et, X = S

Scheme

The electrochemical properties of the new compounds were studied by cyclic voltammetry (CV) and the data are collected in Table 1. All the voltammograms show two reversible one-electron oxidation waves, corresponding to the TTF moiety, and one irreversible reduction wave, corresponding to the acceptor moiety. (The sharpening of the reduction wave associated with E^2_{ox} is quite common in CV of TTF derivatives when CH_2Cl_2 is used as a solvent and has been attributed to adsorption phenomena at the electrode [16]). Derivatives **5c**, **6c** and **7c** (Figure 1) show a less negative reduction potential, in agreement with the stronger electron-acceptor character of the thiobarbiturate end group, when compared to its barbiturate analogues.

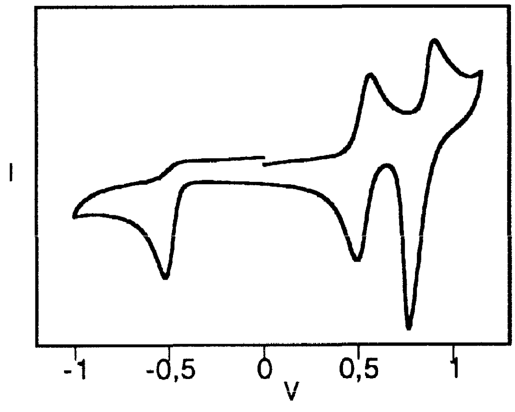


Figure 1. Cyclic voltammogram of **7c**.

Thermal stability is an important requirement for the incorporation of new chromophores in poled-polymer structures [9]. Derivatives **5**, **6** and **7** show a good degree of thermal stability, as evidenced by their decomposition temperatures (T_d) (Table 1).

The UV-Vis spectra of new chromophores were registered in the same solvent (DMSO) used in EFISH measurements. The position of the lowest energy absorption band is given in Table 1. It can be seen that the replacement of the barbiturate group in compounds **a** and **b** for a thiobarbiturate moiety (compounds **c**) results in marked bathochromic shifts. The observed hypsochromic shift of the lowest energy absorption band on increasing the number of double bonds (n) is noteworthy. Studies in order to clarify this unusual phenomenon are being pursued.

$\mu\beta$ values of the title compounds were measured using the electric-field-induced second harmonic (EFISH) generation technique, in DMSO as a solvent, since the limited solubility of some of these derivatives precluded a comparative study in other solvents. Measurements were performed at a fundamental wavelength of 1,907 nm in order to minimize possible enhancements of the nonlinear response due to resonance effects. Inspection of Table 1 reveals that $\mu\beta$ values increase in the series **a**<**b**<**c** and **5**<**6**<**7**, showing the beneficial effects of the thiobarbiturate end group and the extended conjugated chain on the molecular first hyperpolarizability (β). The zero-frequency hyperpolarizability ($\mu\beta_0$) values were obtained from a two-level dispersion model [17,18] and are also shown in Table 1.

Table 1
UV-Vis, redox potentials, decomposition temperatures and $\mu\beta$ values for **5**, **6** and **7**

Compound	λ_{max} [a]	E^1_{ox} [b]	E^2_{ox} [b]	E_{red} [b]	T_d [c]	$\mu\beta$ [d]	$\mu\beta_0$ [d]
5a	641	0.55	0.80	-0.76	234	80	39
5b	650	0.58	0.92	-0.78	221	142	67
5c	716	0.60	0.97	-0.63	194	480	180
6a	597	0.61	0.82	-0.67	248	190	104
6b	609	0.59	0.97	-0.70	227	290	154
6c	661	0.60	1.00	-0.57	195	760	347
7c	646	0.56	0.90	-0.52	206	960	455

[a] In nm, DMSO as solvent.

[b] In Volts *vs.* Ag/AgCl, 0.1M TBA ClO_4/CH_2Cl_2 (DMF for **5a** and **6a**), glassy carbon electrode, scan rate 200 mV.s^{-1}.

[c] In °C. Determined by TGA-DTA, except for **5b**, **6a** and **6c** (DSC).

[d] All $\mu\beta$ values in (10^{-48} esu) units. Measured in DMSO at 1,907 nm.

Semiempirical calculations (FF-PM3) were also carried out and showed a reasonable agreement between the calculated and experimental $\mu\beta_0$ values. Thus, calculations on **5a**, **6a**, and model compounds **5d**, **6d** and **7d** (R = H, X = S, n = 0, 1 and 2, respectively) gave $\mu\beta_0$ values of 103, 164, 177, 296 and 544 (.10^{-48} esu) respectively, which clearly reproduce the observed trends in EFISH experiments. The same qualitative agreement was found in AM1 calculations, but this method largely overestimated the calculated values, which confirms the good parametrization of PM3 for TTF-type compounds [19]. These calculations also show the overlap between the HOMO and LUMO, which is a requisite for obtaining good second-order responses in push-pull polyenes [20] (Figure 2).

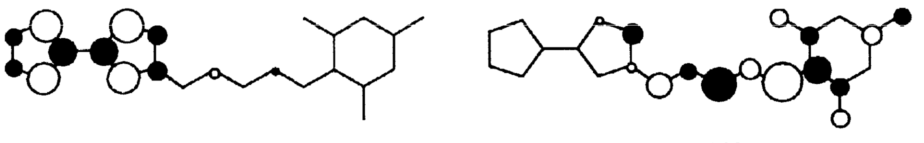


Figure 2. HOMO and LUMO of **7d**

Geometry optimization (PM3) of **6a** and **6d** revealed that these compounds are planar and that the corresponding average bond length alternations (BLA) are -0.094 and -0.092, respectively. These values agree with the fact that the experimentally determined β values are positive [21,22], and indicate that BLA is high (more pronounced near the TTF end than near the acceptor end), although slightly decreases on introduction of the more powerful electron-acceptor thiobarbituric group. On the other hand, calculated BLA values for an isolated molecule usually afford a more alternated structure than those found either in the solid state or in solution [9]. In fact, the ^{1}H-NMR spectrum (CS_2) of **6c** reveals a difference (ΔJ) between CH=CH and CH-CH $^3J_{HH}$ coupling constants of only 2.6 Hz, which is intermediate between that of fully alternated polyenes (≈ 6.5 Hz) and cyanines (0 Hz) [23]. This result indicates that the contribution of the zwitterionic form to the ground state of **6c** is greater than predicted by theoretical calculations and agrees with cyclovoltammetric data, which show the strong electron-withdrawing effect of the acceptor end group in compounds **c**.

In conclusion, TTF-π-(thio)barbituric systems are efficient NLO chromophores displaying good thermal stabilities. These features make them potential candidates for incorporation in poled-polymers. Results along these lines will be reported in due course.

Acknowledgements. We are indebted to DGICYT (Projects PB94-0577 and PB95-0428-CO2) and CICYT (Project MAT96-1073-CO2-01) for financial support.

References

[1] Prasad PN, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers. New York: Wiley, 1991.

[2] Denning RG. J. Mater. Chem. 1995;5:365-378.

[3] Marder SR, Kippelen B, Jen AK-Y, Peyghambarian N. Nature 1997;388:845-851.

[4] Verbiest T, Houbrechts S, Kauranen M, Clays K, Persoons A. J. Mater. Chem. 1997;7:2175-2189.

[5] Alain V, Fort A, Barzoukas M, Chen C-T, Blanchard-Desce M, Marder SR, Perry JW. Inorg. Chim. Acta 1996;242:43-49.

[6] Shu C-F, Tsai WJ, Chen J-Y, Jen AK-Y, Zhang Y, Chen T-A. Chem. Commun. 1996:2279-2280.

[7] Bublitz GU, Ortiz R, Runser C, Fort A, Barzoukas M, Marder SR, Boxer SG. J. Am. Chem. Soc. 1997;119:2311-2312.

[8] Jen AK-Y, Cai Y, Bedworth PV, Marder SR. Adv. Mater. 1997;9:132-135.

[9] Blanchard-Desce M, Alain V, Bedworth PV, Marder SR, Fort A, Runser C, Barzoukas M, Lebus S, Wortmann R. Chem. Eur. J. 1997;3:1091-1104.

[10] de Lucas AI, Martín N, Sánchez L, Seoane C, Garín J, Orduna J, Alcalá R, Villacampa B. Tetrahedron Lett. 1997;38:6107-6110.

[11] Jen AK-Y, Rao VP, Drost KJ, Wong KY, Cava MP. J. Chem. Soc., Chem. Commun. 1994:2057-2058.

[12] Andreu R, de Lucas AI, Garín J, Martín N, Orduna J, Sánchez L, Seoane C. Synth. Met. 1997;86:1817-1818.

[13] de Lucas AI, Martín N, Sánchez L, Seoane C, Andreu R, Garín J, Orduna J, Alcalá R, Villacampa B. Tetrahedron, submitted.

[14] Garín J, Orduna J, Uriel S, Moore AJ, Bryce MR, Wegener S, Yufit DS, Howard JAK. Synthesis 1994:489-493.

[15] González M, Martín N, Segura JL, Garín J, Orduna J. Tetrahedron Lett., submitted.

[16] Fourmigué M, Huang Y-S. Organometallics 1993;12:797-802.

[17] Oudar JL. J. Chem. Phys. 1977;67:446-457.

[18] Oudar JL, Chemla DS. J. Chem. Phys. 1977;66:2664-2668.

[19] Batsanov AS, Bryce MR, Heaton JN, Moore AJ, Skabara PJ, Howard JAK, Ortí E, Viruela PM, Viruela R. J. Mater. Chem. 1995;5:1689-1696.

[20] Kanis DR, Ratner MA, Marks TJ. Chem. Rev. 1994;94:195-242.

[21] Marder SR, Cheng L-T, Tiemann BG, Friedli AC, Blanchard-Desce M, Perry JW, Skindhøj J. Science 1994;263:511-514.

[22] Marder SR, Gorman CB, Meyers F, Perry JW, Bourhill G, Brédas J-L, Pierce BM. Science 1994;265:632-635.

[23] Scheibe G, Seiffert W, Hohlneicher G, Jutz Ch, Springer HJ. Tetrahedron Lett. 1966:5053-5059.