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Synthesis and non-linear optical and redox properties of 6-nitro-6′-piperidyl-2,2′-bisbenzothiazole: a new type of push–pull molecules

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Abstract—The present paper describes the synthesis, the non-linear optical and redox properties of 6-nitro-6′-piperidyl-2,2′-bisbenzothiazole, the first described member of a new family of push–pull structures based in the 2,2′-bisbenzothiazole.

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1. Introduction

Our research on new organic materials includes an interest in new molecules with non-linear optical (NLO) properties[1] and other dipolar moment-dependent properties. Organic molecules with large delocalized π-electron systems are good candidates for the display of large non-linear responses.[2] The main factor involved in presenting such properties is the presence and nature of electron-donating and -accepting groups. Furthermore, the extension and kind of conjugation path is crucial for the transfer of charge between the substituents in the presence of electric fields. A number of factors prompted us to synthesize and study the properties of 6-nitro-6′-piperidyl-2,2′-bisbenzothiazole (**1**): (a) our experience in the chemistry of benzothiazoles and 2,2′-bisbenzothiazoles,[3] (b) the scarce mention in the literature of related systems,[4] (c) the high thermal stabilities of systems derived from benzothiazole, characteristic very adequate for possible technological applications of this molecules, and (d) the good theoretical value for $\beta(0)$ (34×10^{-30} esu) predicted for **1**,[5] similar to the described[6] for 4-(*N*,*N*-dimethylamino)-nitrostilbene (DANS) ($\beta(0)=55\times10^{-30}$ esu).

2. Results and discussion

Scheme 1 shows the synthetic path followed to prepare **1**. The strategy was to prepare the two benzothiazoles conveniently functionalized and link both by a coupling reaction. The first half of the molecule was prepared from 4-(*N*-piperidyl)aniline. The problem of the construction of substituted benzothiazoles consists in the formation of the corresponding 2-aminothiophenol from the adequate aniline. Several procedures[7] for performing this process are known but in general the yields are low, the manipulation difficult, or the methods incompatible with various functional groups. The only method that proved adequate in our case is the one described by Levkoev et al.[8] This method consists in reacting aniline and sodium thiosulfate in an oxidative medium. The second half-molecule was prepared by means of a standard Sandmeyer reaction[9] from commercial 2-amino-6-nitrobenzothiazole. Finally, the coupling reaction was done via reaction of the organozinc derivative of 6-(*N*-piperidyl)benzothiazole with the above bromoderivative.[10] The yields from this reaction are never high and the formation of some amount of the symmetric compound 6,6′-di(*N*-piperidyl)2,2′ bisbenzothiazole in unavoidable.

After preparing the desired compound, we studied its non-linear optic behavior by means the EFISH method, which permitted the calculation $\mu\beta(0)$ from the experimental value of $\mu\beta$ by using a simple two-level model.[11] The low solubility of **1** in the common organic solvents prevented us from determining the dipolar moment, μ; hence in this

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Keywords: 2,2′-Bisbenzothiazole; Synthesis; Push–pull molecules; Non-linear optical properties; Redox properties.

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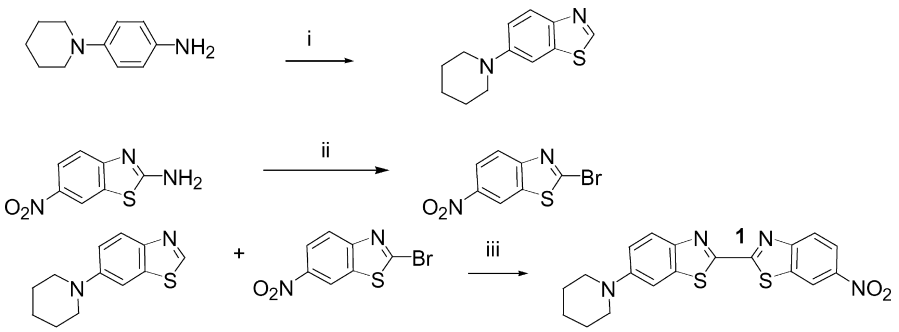


Scheme 1. *Reagents and conditons.* (i) $Na_2S_2O_3{\cdot}5H_2O$, $K_2Cr_2O_7$, AcOH, 0 °C, 8 h, r.t. ovemigth, 34%. (ii) $NaNO_2$, CuBr, HBr 48%. (iii) Bu–Li, anh. $ZnCl_2$, CuI.

paper the experimental results are expressed as $\mu\beta$ (375×10^{-48} esu) and $\mu\beta(0)$ (276×10^{-48} esu) in CH_2Cl_2 (λ=1.9 μm, static electric field=5 kV). Our calculated theoretical value for $\beta(0)$ is 34×10^{-30} esu, and for μ is 8.3×10^{-18} esu; consequently, the theoretically estimated value for $\mu\beta(0)$ is 283×10^{-48} esu. The concordance between this value and the experimental one is excellent, showing that the semiempirical method (AM1-RHF) used is very adequate in this kind of molecules.

To study the redox properties of **1**, we applied two complementary techniques: cyclic voltamperommetry and EPR.

As can be seen in Figure 1a, the cyclic voltammogram for the reduction of **1** in CH_2Cl_2 solution with tetrabutylammonium perchlorate (0.1 M) as electrolyte on Pt at 25 °C displayed two consecutive quasi-reversible one-electron redox couples, with standard potentials $E_1^o=-1.07$ V and $E_2^o=-1.46$ V vs SSCE (NaCl-saturated calomel electrode). Both peaks had the same cathodic and anodic heights and showed an increasing difference between their corresponding anodic and catodic peak potentials ($E_p^a-E_p^c$) from 0.10 V at a scan rate (ν) of 20 mV s^{-1} to 0.17 V at ν=200 mV s^{-1}. They can be ascribed to the equilibrium processes $\mathbf{1}+e^- \leftrightarrow \mathbf{1}^{\cdot-}$ and $\mathbf{1}^{\cdot-}+e^- \leftrightarrow \mathbf{1}^{2-}$. Similar results were obtained using DMF as solvent, indicating a large stability of the radical anion $\mathbf{1}^{\cdot-}$ and the dianion $\mathbf{1}^{2-}$ in both media. For the oxidation of the same solutions, their cyclic voltammograms exhibited an anodic irreversible peak either in DMF or in CH_2Cl_2 for $\nu<50$ mV s^{-1}. At higher scan rates in CH_2Cl_2 solution, its associated cathodic peak was already observed, the process behaving $\mathbf{1} \leftrightarrow \mathbf{1}^{\cdot+}+e^-$ as a quasi-reversible one-electron redox pair (($E_p^a-E_p^c$)=0.12 V at ν=200 mV s^{-1}) with a standard potential E^o=0.95 V vs SSCE (Fig. 1b). These results indicate the electron accepting and donating ability of **1**, the radical cation species being of much lower stability than the radical anion.

The above cyclic-voltammetric behavior was confirmed by electron paramagnetic resonance (EPR) spectroscopy. So, while $\mathbf{1}^{\cdot-}$ was easily detected by chemical reduction (see Section 4), we were not able to detect $\mathbf{1}^{\cdot+}$.

To characterize the EPR spectrum of $\mathbf{1}^{\cdot-}$, we had previously registered the spectra of the radical anions chemically derived from 6-nitrobenzothiazole (**2**) and 2,2′-bisbenzothiazole (**3**). A multiplet of lines (g=2.0052; peak to peak linewidth, ΔH_{pp}=0.2 G) of a very stable radical was obtained when a degassed DMSO solution of **2** was treated with potassium *t*-butoxide at room temperature (Fig. 2a).

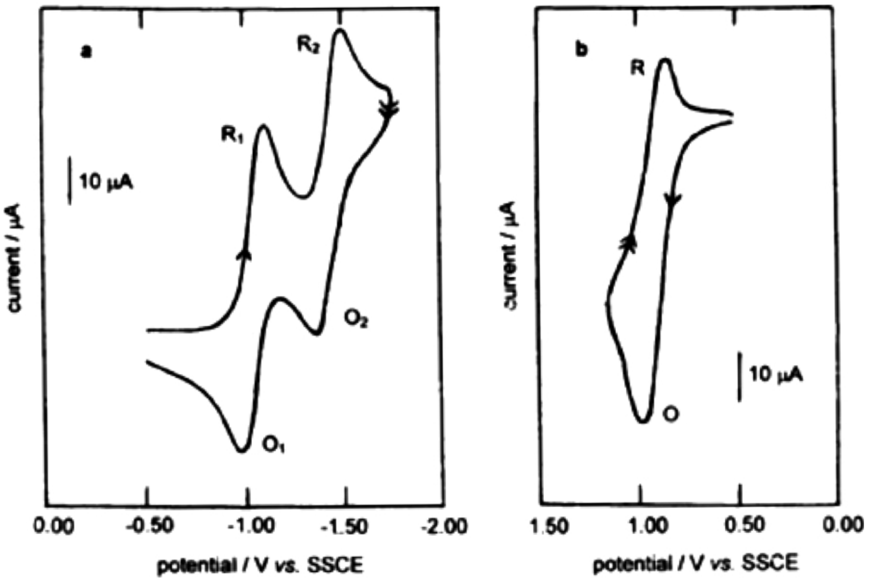


Figure 1. Cyclic voltammograms for the (a) reduction and (b) oxidation of a 1 mM **1** solution in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate at 200 mV s^{-1} and at 25 °C on a 0.093 cm^2 Pt electrode. Initial potential: (a) −0.50 V, (b) 0.50 V. Reversal potential: (a) −1.800 V, (b) 1.200 V.

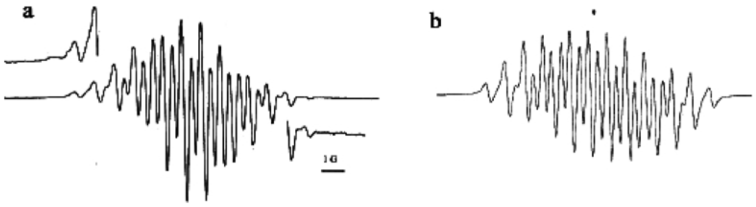


Figure 2. (a) EPR spectrum of $2^{\cdot-}$ in DMSO solution at room temperature. (b) Computer simulation with the values given in Table 1.

The intensity of the lines slightly increased with short periods of ultraviolet irradiation.

This spectrum (Fig. 2b) was simulated[12] using the hyperfine splitting (hfs) values showed in Table 1, and was attributed to $\mathbf{2}^{\cdot-}$. The assignment of hfs values to the different nuclei in the molecule was verified by molecular orbital calculations, using the semiempirical MINDO/3 method as shown also in Table 1.

Anion radicals from thiazolyl derivatives have already been detected and well characterized by EPR;[13] however, as far as we know, no spectra of the reduced species from benzothiazolyls have been reported to date. Our attempts to generate the anion radical from the parent compound benzothiazole or from 6-morpholinebenzothiazole, a benzothiazole with a secondary amine as substituent, were unsuccessful. Therefore, the presence of an electron withdrawing group such as the nitro group is necessary to facilitate the electron transfer reaction and to stabilize the corresponding charged species.

Similarly, when degassed DMSO solution of 2,2′-bisbenzothiazole (**3**), treated with potassium *t*-butoxide, were prolonged irradiated (1 h) with UV light a persistent multiplet of very narrow lines (g=2.0043; ΔH_{pp}=0.09 G) was detected by EPR (Fig. 3a). This spectrum (Fig. 3b) was simulated by using the hfs values displayed in Table 1 and was attributed to $\mathbf{3}^{\cdot-}$. As before, the assignment was performed by MINDO/3. Two different conformations could be expected for 2,2′-bisbenzothiazole, however the spectrum at room temperature revealed the presence of only one radical species. As in the case of 2,2′-bisthiazole, the free rotation around C–C bond is hindered in the neutral molecule, and the energy barrier to rotation expected for the anion radical should be larger considering the partial double bond character, similar as it is suggested in 2,2′-bisthiazole by Pedully et al.[13] The consequence is the presence of only one isomer in solution.

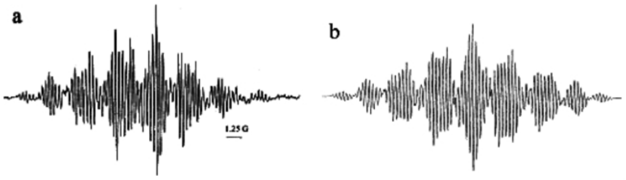
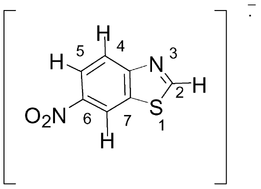


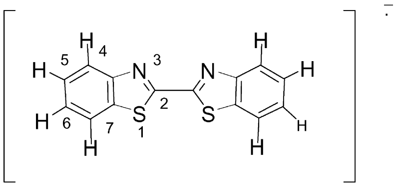
Figure 3. (a) EPR spectrum of $3^{\cdot-}$ in DMSO solution at room temperature. (b) Computer simulation with the values given in Table 1.

When a degassed solution of 6-nitro-6′-(*N*-piperidy)-2,2′-bisbenzothiazole (**1**) ($\sim 10^{-2}$ M) in THF–DMSO (1:1) with an excess of potassium *t*-butoxide was irradiated with UV light, a symmetric multiplet of lines centered at g=2.0048 was detected by EPR (Fig. 4a). This radical species was stable and was attributed to $\mathbf{1}^{\cdot-}$. One of the simulations which roughly fits to the experimental spectrum (Fig. 4b) was performed by using the following hfs values in gauss: a(N)=6.87, a(N)=2.87, a(1H)=2.20, a(1H)=1.94, a(3H)=0.9, ΔH_{pp}=0.7 G. Values from other nuclei in the molecule should be less than the linewidth. As before, the presence of only one radical species suggests only one isomer in solution at room temperature.

Table 1. Experimental and calculated hyperfine coupling constants (a) for radical anions derived from 6-nitrobenzothiazole (**2**) and 2,2′-bisbenzothiazole (**3**)



$\mathbf{2}^{\cdot-}$



$\mathbf{3}^{\cdot-}$

	a (exp)[a]	a (theor)[b]		a (exp)[a]	a (theor)[b]
$\mathbf{2}^{\cdot-}$	1.7(N3)	614	$\mathbf{3}^{\cdot-}$		684
	0.85(N6)	511		3.34(N3,N3′)	806
	2.02(H2)	1175		2.16(H4,H4′)	718
	0.85(H4)	670		0.56(H5,H5′)	791
	0.85(H5)	898		1.88(H6,H6′)	672
	1.28(H7)	1110		0.28(H7,H7′)	

[a] In Gauss.

[b] Arbitrary units.

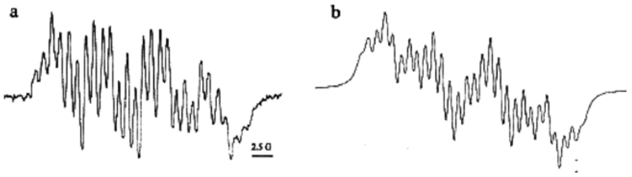


Figure 4. (a) EPR spectrum of $\mathbf{1}^{\cdot -}$ THF–DMSO (1:1) solution at room temperature. (b) Computer simulation with the values given in the text.

3. Conclusion

We report the first synthesis of 6-nitro-6′-(*N*-piperidy)-2,2′-bisbenzothiazole, a new push–pull molecule. This molecule shows good NLO properties and a dual, oxidative and reductive, three-stage single-electron redox character. It shows a quite stable radical anion detected by EPR. Related to this radical anion, the first EPR spectra of radical anions derived from bisbenzothiazoles is also described

4. Experimental

4.1. General

Melting points were determined using a Köfler apparatus provided with a Reichert Thermovar microscope and are uncorrected. TLC was carried out on SiO_2 (Alugram SIL G/UV_{254} Macherey–Nagel 0.25 mm) and spots were located with UV light. Flash chromatography was carried out on SiO_2 (Silica Gel 60 A CC, Merck). Organic extracts were dried over anhydrous $MgSO_4$, and solutions were evaporated under reduced pressure with a rotatory evaporator. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. NMR spectra were measured with Varian Gemini-200 (200 MHz) and Varian Unity-300 (300 MHz) spectrometers; data are given in δ/ppm, referenced to TMS for ^{1}H NMR, to $CDCl_3$ (77.0 ppm) for ^{13}C NMR and J values are given in Hz. Mass spectra were measured in chemical impact (CI, NH_3) mode with a Hewlett–Packard 5988A spectrometer, or with a Fisons VG-Quattro spectrometer. The samples were then introduced into a matrix of 2-nitrobenzyl alcohol for FAB analysis and subjected to bombardment with cesium atoms.

4.1.1. Electron spin resonance of radical anions from 6-nitro-6′-piperidyl-2,2′-bisbenzothiazole (1), 6-nitrobenzothiazole (2) and 2,2′-bisbenzothiazole (3). (a) *Preparation of the samples*: solutions of **1**, **2** and **3** (10^{-2} M) in dimethylsulfoxide in a quartz tube were degassed by bubbling argon while an excess of dimethylsulfoxide solution of potassium *t*-butoxide was added. These colored solutions were introduced into the cavity of the spectrometer at room temperature and their spectra were registered while irradiated with light from a high-pressure mercury lamp (500 W).

(b) EPR spectra were recorded with a Varian E-109 spectrometer working in the X band. Determinations of the g values of the radicals were made with DPPH (g=2.0037) as standard.

4.1.2. Synthesis of 6-(*N*-piperidyl)benzothiazole. Dihydrogensulfate of *N*-(4-aminophenyl)piperidine (1.59 g, 4.25 mmol) and sodium thiosulfate pentahydrate (2.04 g, 8.23 mmol) were dissolved in 18% aqueous solution of acetic acid (3.2 mL) at 0 °C. A solution of potassium dichromate (411 mg, 1.40 mmol) in diluted acetic acid (6.5%, 8.3 mL) was added for 1 h. The reaction mixture was stirred in an ice bath for 8 h and overnight at room temperature. The formed precipitate was filtered, washed with water, suspended in formic acid (15 mL) and heated under reflux for 3 h. The formic acid was removed, the residue diluted with water (15 mL), neutralized with sodium bicarbonate and extracted with methylene chloride. The solvent was removed and 6-(*N*-piperidyl)benzothiazole (305 mg, 34%) was isolated as a white solid by column chromatography over silicagel, eluting with CH_2Cl_2–$EtOOCCH_3$ 9:1; mp 87–88 °C; TLC (SiO_2, CH_2Cl_2–$EtOOCCH_3$ 9:1); R_f=0.34; IR (KBr): ν=2935, 2854 (C–H st.); 1600, 1542 (arom.); 1480, 1383 (thiazole); 1237 (C–N st.); 940, 876, 824 (C_{ar}–H) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, TMS_{int}): δ=8.72 (s, H^6, 1H), 7.93 (d, H^4, J_{3-4}=9.2 Hz, 1H), 7.34 (d, H^1, J_{1-3}=2.2 Hz, 1H), 7.17 (dd, H^3, J_{1-3}=2.2 Hz, J_{3-4}=9.2 Hz, 1H), 3.19 (t, H^8, J_{8-9}=5.4 Hz, 4H), 1.71 (sc, H^9, J_{8-9}=5.4 Hz, 4H), 1.59 (sc, H^{10}, 2 H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.49 (C^6), 146.50 (C^5), 135.21 (C^7), 123.30 (C^4), 117.83 (C^3), 107.11 (C^1), 51.32 (C^8), 25.81 (C^9), 24.20 (C^{10}) ppm; MS (70 eV, CI, NH_3): m/z: 219 $[M+1]^+$.

4.1.3. Synthesis of 2-bromo-6-nitrobenzothiazole. 2-Amino-6-nitrobenzothiazole (5 g, 25.6 mmol) was mixed under vigorous stirring with 85% phosphoric acid (23 mL) at 50 °C. The solution was cooled to −20 °C and a solution of sodium nitrite (1.91 g) and water (2.2 mL) was slowly added. After 1 h, the resulting suspension was poured over a solution of cuprous bromide (4.51 g, 31.4 mmol) in 48% hydrobromic acid (25 mL) at room temperature and mechanically stirred. After 1 h, the mixture was heated at 40 °C for 2 h, diluted to a final volume of 500 mL and extracted repeatedly with methylene chloride. The organic layer was dried over anhydrous magnesium sulfate, the solvent removed and 2-bromo-6-nitrobenzothiazole (4.66 g, 70%) isolated as an orange solid; mp 202–204 °C dec. (lit. 206–7 °C); TLC (SiO_2, CH_2Cl_2); R_f=0.46; IR (KBr): ν=3100 (C_{ar}–H st.); 1601, 1568 (sis. arom.); 1510 (C_{ar}–NO_2 st. as.); 1344 (C_{ar}–NO_2 st. si.); 884, 843, 751 (C_{ar}–H) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, TMS_{int}):-$\delta_{=8.76\ (\mathrm{d},\ \mathrm{H}}{}^{1}$, J_{1-3}=1.2 Hz, 1H), 8.35 (dd, H^3, J_{1-3}=1.2 Hz, J_{3-4}=9.2 Hz, 1H), 8.08 (d, H^4, J_{3-4}=9.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=155.89 (C^5), 145.33 (C^2), 144.67 (C^7), 137.69 (C^6), 123.19 (C^4), 122.14 (C^3), 117.37 (C^1) ppm.; MS (70 eV, CI, CH_4): m/z=259, 261 $[M+H^+]$.

4.1.4. Synthesis of 6-nitro-6′-piperidyl-2.2′-bisbenzothiazole. 6-(*N*-piperidyl)benzothiazole (2.40 g, 11.0 mmol) was dissolved in anhydrous tetrahydrofurane (35 mL) under inert atmosphere and at −100 °C. Over this solution butyllithium (7,5 mL 1.6 M in hexane, 12.0 mmol) was slowly added. After addition, the mixture was stirred in the same condition for further 20 min and anhydrous zinc chloride (1.67 g, 12.2 mmol) in anhydrous tetrahydrofurane (15 mL) was added. The reaction mixture was maintained for 40 min and 2-bromo-6-nitrobenzothiazole (2.90 g, 11.2 mmol), dichlorobis(triphenylphosphine)palladium(II) (488 mg, 0.70 mmol) and cuprous iodide (353 mg, 1.85 mmol) were added in this order and in solid state. The mixture was heated for 15 h at 50 °C. The solvent was removed, and the residue was treated with hydrochloric acid (250 mL 0.1 M). The aqueous layer was extracted repeatedly with methylene chloride, the organic layer dried with anhydrous magnesium sulfate, filtered and the solvent was removed. 6-nitro-6$'$-piperidyl-2.2$'$-bisbenzothiazole was isolated as a red solid (1.41 g, 32%) by column chromatography over silicagel, eluting with CH_2Cl_2–$EtOOCCH_3$ in a gradient from 10:0 to 9:1. The product was purified for elemental analysis by sublimation at 280 °C and 0.5 mm Hg; mp 298–300 °C; TLC (SiO_2, CH_2Cl_2–$EtOOCCH_3$ 30:1); R_f=0.48; IR (KBr): ν=3115 (C_{ar}–H st.); 2937, 2860 (C–H st.); 1603, 1546 (sis. arom.); 1517 (C_{ar}–NO_2 st. as.); 1453, 1383 (thiazol); 1337 (C_{ar}–NO_2 st. si.); 1229 (C–N st.); 895, 858, 814 (C_{ar}–H) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS_{int}): δ=8.83 (d, H^8, J_{8-10}=2.4 Hz, 1H), 8.34 (dd, H^{10}, J_{8-10}=2.4 Hz, J_{10-11}=8.7 Hz, 1H), 8.13 (d, H^{11}, J_{10-11}=8.7 Hz, 1H), 7.94 (d, H^4, J_{3-4}=9.0 Hz, 1H), 7.28 (d, H^1, J_{1-3}=2.4 Hz, 1H), 7.19 (dd, H^3, J_{1-3}=2.4 Hz, J_{3-4}=9.0 Hz, 1H), 3.32 (t, H^{15}, J_{15-16}=5.4 Hz, 4H), 1.73 (sc, H^{16}, J_{15-16}=5.4 Hz, 4H), 1.65 (sc, H^{17}, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=167.46 (C^{12}), 157.28 (C^{13}), 155.37 (C^6), 151.50 (C^9), 146.67 (C^5), 145.37 (C^2), 138.73 (C^{14}), 135.81 (C^7), 124.52 (C^{11}), 123.68 (C^4), 122.03 (C^{10}), 118.42 (C^8), 117.95 (C^3), 105.49 (C^1), 50.19 (C^{15}), 25.62 (C^{16}), 24.23 (C^{17}) ppm; UV (CH_2Cl_2): $\lambda_{máx}$ (nm)/ε (M^{-1} cm^{-1})=450/2,6×10^4, 347/1,0×10^4, 302/1,5×10^4; MS-FAB(+): m/z=396 ($M^{\cdot+}$); elemental analysis: found C: 57.55%, H: 3.94%, N: 14.20%, S: 16.12%, $C_{19}H_{16}N_4O_2S_2$ requires C: 57.57%, H: 4.07%, N: 14.13%, S: 16.17%).

Acknowledgements

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