

Zwitterionic 3-(1,3-Dithiol-2-yl)phenolates

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A new class of zwitterionic 3-[2-(dialkylamino)-1,3-dithiol-2-yl]phenolates has been synthesized by the heterocondensation of the corresponding phenacyl carbodithioates. These compounds have been synthesized following a three steps procedure that involves the reaction of 2-bromo-1-(3-hydroxyphenyl)ethanone with various salts of dithiocarbamic acids, heterocyclocondensation under acidic conditions and treatment with weak aqueous bases. The zwitterionic phenolates exhibit intramolecular charge transfer.

Keywords: dithiocarbamates, 1,3-dithiolium salts, regioselective bromination, zwitterionic compounds

1,3-Dithiolium salts can be used as building blocks in the synthesis of tetrathiafulvalenes (TTF) [1-4], the later being good π -electron donors for metals [5, 6]. More than that, some new studies focus on TTFs as donor groups in intramolecular charge-transfer complexes [7, 8]. Concerning acceptor moieties, pyridinium and bipyridium cations have received a great deal of attention [9-16]. Many studies focus on systems where the donor and acceptor moieties are linked through a σ - and/or π -bonded bridge [17-21]. Investigations performed on (1,3-dithiolium-2-yl)phenolates systems revealed that 1,3-dithiolium cations can act as acceptor groups in intramolecular charge-transfer processes. With recent reports made by our group concerning the synthesis of some 4-(hydroxyaryl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts from the 1-(2-hydroxyaryl)ethanones and propan-1-ones [22, 23], we

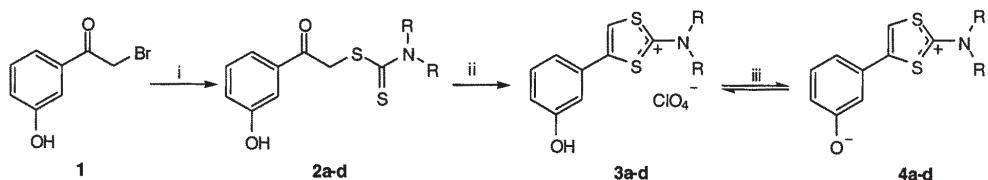
wish to extend our studies by presenting a new class of zwitterionic 3-(1,3-dithiolim-2-yl)phenolates and the 4-(3-hydroxyaryl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts used to obtain them.

Experimental part

a. Analysis methods

Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. UV-Vis spectra were recorded on a Varian BioCarry 100 Spectrophotometer. NMR spectra were recorded on a Bruker DPX-300 Spectrometer. Chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N, S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement ($\pm 0.3\%$) with the calculated values.

b. Synthesis



i. $\text{R}_2\text{NC}(\text{S})\text{S}^-$, acetone, reflux; ii. $\text{H}_2\text{SO}_4/\text{AcOH}$ 1:3 (v/v), 80 °C, 70% HClO_4 ; iii. NaHCO_3 (aq)

2, 3, 4	R	R
a	CH ₃	CH ₃
b	CH ₂ CH ₃	CH ₂ CH ₃
c	(CH ₂) ₅	
d	(CH ₂) ₂ -O-(CH ₂) ₂	

Scheme 1. Synthesis of dithiocarbamates **2**, 1,3-dithiolium perchlorates **3** and zwitterionic phenolates **4**

1-(3-Hydroxyphenyl)-1-oxaethan-2-yl-piperidine-1-carbodithioate (**2c**): General Procedure

To a solution of 2-bromo-1-(3-hydroxyphenyl)ethanone (**1**, 2.15 g, 0.01 mol) in acetone (30 mL), a solution of piperidinium piperidine-1-carbodithioate (2.46 g, 0.01 mol) in acetone-water (1:1, 15 mL) was added. The reaction

mixture was heated at reflux for 15 min, cooled to room temperature and then poured in water. The precipitate was filtered, washed with water and dried off. Recrystallization from EtOH (50 mL) gave colorless crystals; yield 2.21 g (75%). Analytical and spectral data of carbodithioates **2** are presented in table 1.

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	M.p., °C	η, %	IR-ATR, cm ⁻¹	NMR (DMSO- <i>d</i> 6)
2a	140 - 141	68	3347, 2948, 1655, 1583, 1486, 1428, 1270, 1210, 1149, 979, 770, 743, 680	¹ H NMR δ : 3.65 (6H, s, 2CH ₃); 4.82 (2H, s, CH ₂); 7.04 (1H, m, H-4); 7.21 (1H, m, H-6); 7.42 (1H, m, H-5); 7.46 (1H, m, H-2); 9.15 (1H, s, OH). ¹³ C NMR δ : 41.8, 44.0, 45.2, 113.8, 120.1, 120.5, 130.8, 138.4, 157.9, 191.8, 195.6
2b	135 - 136	62	3341, 2980, 1654, 1580, 1494, 1423, 1272, 1204, 1141, 982, 776, 746, 682	¹ H NMR δ : 1.24 (3H, t, CH ₃); 1.33 (3H, t, CH ₃); 3.89 (4H, q, 2CH ₂ -N); 4.81 (2H, s, CH ₂); 7.05 (1H, m, H-4); 7.23 (1H, m, H-6); 7.42 (1H, m, H-5); 7.45 (1H, m, H-2); 9.34 (1H, s, OH). ¹³ C NMR δ : 11.6, 12.8, 43.7, 47.5, 48.1, 113.1, 120.5, 120.7, 130.1, 138.1, 158.2, 191.0, 195.1
2c	177-178	75	3350, 2931, 1657, 1580, 1481, 1434, 1314, 1274, 1224, 1163, 970, 886, 768, 749, 679	¹ H NMR δ : 1.65 (6H, m, 3CH ₂); 4.09 (4H, m, 2CH ₂ -N); 4.81 (2H, s, CH ₂); 7.03 (1H, m, H-4); 7.20 (1H, m, H-6); 7.42 (1H, m, H-5); 7.45 (1H, m, H-2); 9.31 (1H, s, OH). ¹³ C NMR δ : 23.4, 25.2, 25.6, 43.6, 51.1, 52.2, 113.7, 119.8, 120.3, 130.5, 138.2, 157.2, 191.1, 195.9
2d	160 - 161	70	3281, 2970, 1682, 1586, 1421, 1266, 1226, 1105, 1026, 986, 680	¹ H NMR δ : 3.81 (4H, m, CH ₂ OCH ₂); 4.20 (4H, m, CH ₂ NCH ₂); 4.88 (2H, s, CH ₂); 7.04 (1H, m, H-4); 7.21 (1H, m, H-6); 7.42 (1H, m, H-5); 7.46 (1H, d, H-2); 9.25 (1H, s, OH). ¹³ C NMR δ : 43.5, 50.4, 51.6, 65.9, 113.1, 120.6, 120.8, 130.7, 138.3, 157.5, 191.1, 195.2

4-(3-Hydroxyphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (3c); General Procedure

To a mixture of sulfuric acid (98%, 1 mL) and glacial acetic acid (3 mL), 1-(3-hydroxyphenyl)-1-oxaethan-2-yl-piperidine-1-carbodithioate (**3c**, 1 g, 3.38 mmol) was added in small portions. The reaction mixture was heated at 80 °C for 10 min. After cooling, HClO₄ (70%, 0.5 mL) and methyl acetate (150 mL) were added in this order to isolate the corresponding perchlorate. The precipitate was filtered and dried off. Recrystallization from EtOH (25 mL) gave colorless crystals; yield 1 g (78%). Analytical and spectral data of 1,3-dithiolium perchlorates **3** are presented in table 2.

3-[2-(Piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (4c); General Procedure

To a saturated sodium hydrogencarbonate solution (20 mL), perchlorate **3c** (1 g, 2.65 mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2 h under vigorous stirring at room temperature, the yellow solid was filtered off, washed with water, and dried. Recrystallization from dichloromethane gave yellow crystals; yield 0.73 g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **4** are presented in table 3.

Results and discussions

A convenient method for the synthesis of 2-(*N,N*-dialkylamino)-1,3-dithiol-2-ylium salts is represented by the

cyclization of the corresponding *N,N*-dialkylamino carbodithioates, compounds that are easily available from 2-bromo-1-(3-hydroxyphenyl)ethanone (**1**) [24].

The synthesis of the 1,3-dithiolium ring can be accomplished following two consecutive reactions as described in scheme 1. 2-Bromo-1-(3-hydroxyphenyl) ethanone (**1**) has been treated with various salts of dialkylaminodithiocarbamic acids in order to provide aminocarbodithioates **2a-d**, in good isolated yields. The structure of dithiocarbamates **2** has been proved by analytical and spectral data (table 1).

Phenacyl carbodithioates are good starting materials for the preparation of various substituted 1,3-dithiolium-2-yl cations under acidic conditions. Using a mixture of concentrated sulfuric acid-glacial acetic acid (1:3 v/v) [25, 26] the cyclization of dithiocarbamates **2a-d** takes place under mild reaction conditions. After 10 min at 80 °C, the homogeneous reaction mixture was cooled to room temperature, 70% perchloric acid was added and then poured into water. Filtration and recrystallization of the precipitate gives 1,3-dithiolium perchlorates **3a-d** as colorless crystals, in good to excellent yields (table 2). The cyclization of dithiocarbamates **2** is accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1650 cm⁻¹) and the presence of a new, strong and broad, absorption band at ca. 1080 cm⁻¹, corresponding to the perchlorate anion. ¹H NMR spectra of 1,3-dithiolium-2-yl perchlorates indicate the absence of the

	M.p., °C	η, %	IR-ATR, cm ⁻¹	NMR (DMSO- <i>d</i> 6)
3a	165-166 dec.	74	3571, 3110, 1561, 1520, 1440, 1248, 1061, 618	¹ H NMR δ : 3.79 (6H, s, 2CH ₃); 6.94 (1H, m, H-5); 7.03 (1H, m, H-2); 7.09 (1H, m, H-4); 7.36 (1H, m, H-6); 7.90 (1H, s, H-5); 9.90 (1H, s, OH). ¹³ C NMR δ : 47.3, 47.7, 112.5, 120.1, 122.6, 130.1, 133.8, 138.7, 139.9, 154.3, 189.4
3b	132-133	70	3578, 3118, 1560, 1521, 1441, 1252, 1063, 620	¹ H NMR δ : 1.39 (6H, t, 2CH ₃); 3.86 (2H, q, CH ₂ -N); 3.96 (2H, q, CH ₂ -N); 6.94 (1H, m, H-5); 7.05 (1H, m, H-2); 7.10 (1H, m, H-4); 7.35 (1H, m, H-6); 7.95 (1H, s, H-5); 9.94 (1H, s, OH). ¹³ C NMR δ : 10.7, 53.4, 54.4, 112.3, 120.5, 122.3, 130.0, 133.4, 138.8, 140.1, 154.9, 189.7
3c	188-189	78	3570, 3124, 1574, 1520, 1410, 1254, 1069, 620	¹ H NMR δ : 1.80 (6H, m, 3CH ₂); 3.86 (4H, m, 2CH ₂ -N); 6.95 (1H, m, H-5); 7.04 (1H, m, H-2); 7.09 (1H, d, H-4); 7.35 (1H, m, H-6); 7.91 (1H, s, H-5); 9.91 (1H, s, OH). ¹³ C NMR δ : 21.5, 24.8, 24.9, 56.1, 57.9, 112.4, 120.0, 122.2, 129.1, 133.7, 138.5, 140.2, 154.8, 189.3
3d	186-187	75	3062, 1550, 1510, 1444, 1242, 1090, 1020, 619	¹ H NMR δ : 3.92 (8H, m, 4CH ₂); 6.94 (1H, m, H-5); 7.03 (1H, m, H-2); 7.10 (1H, d, H-4); 7.35 (1H, m, H-6); 7.85 (1H, s, H-5); 9.82 (1H, s, OH). ¹³ C NMR δ : 54.1, 54.7, 64.6, 112.3, 120.8, 122.4, 130.2, 133.7, 138.8, 140.0, 154.8, 189.1

Table 1
ANALYTICAL AND SPECTRAL DATA OF DITHIOCARBAMATES **2**

	M.p., °C	η, %	IR-ATR, cm ⁻¹	NMR (DMSO- <i>d</i> 6)
3a	165-166 dec.	74	3571, 3110, 1561, 1520, 1440, 1248, 1061, 618	¹ H NMR δ : 3.79 (6H, s, 2CH ₃); 6.94 (1H, m, H-5); 7.03 (1H, m, H-2); 7.09 (1H, m, H-4); 7.36 (1H, m, H-6); 7.90 (1H, s, H-5); 9.90 (1H, s, OH). ¹³ C NMR δ : 47.3, 47.7, 112.5, 120.1, 122.6, 130.1, 133.8, 138.7, 139.9, 154.3, 189.4
3b	132-133	70	3578, 3118, 1560, 1521, 1441, 1252, 1063, 620	¹ H NMR δ : 1.39 (6H, t, 2CH ₃); 3.86 (2H, q, CH ₂ -N); 3.96 (2H, q, CH ₂ -N); 6.94 (1H, m, H-5); 7.05 (1H, m, H-2); 7.10 (1H, m, H-4); 7.35 (1H, m, H-6); 7.95 (1H, s, H-5); 9.94 (1H, s, OH). ¹³ C NMR δ : 10.7, 53.4, 54.4, 112.3, 120.5, 122.3, 130.0, 133.4, 138.8, 140.1, 154.9, 189.7
3c	188-189	78	3570, 3124, 1574, 1520, 1410, 1254, 1069, 620	¹ H NMR δ : 1.80 (6H, m, 3CH ₂); 3.86 (4H, m, 2CH ₂ -N); 6.95 (1H, m, H-5); 7.04 (1H, m, H-2); 7.09 (1H, d, H-4); 7.35 (1H, m, H-6); 7.91 (1H, s, H-5); 9.91 (1H, s, OH). ¹³ C NMR δ : 21.5, 24.8, 24.9, 56.1, 57.9, 112.4, 120.0, 122.2, 129.1, 133.7, 138.5, 140.2, 154.8, 189.3
3d	186-187	75	3062, 1550, 1510, 1444, 1242, 1090, 1020, 619	¹ H NMR δ : 3.92 (8H, m, 4CH ₂); 6.94 (1H, m, H-5); 7.03 (1H, m, H-2); 7.10 (1H, d, H-4); 7.35 (1H, m, H-6); 7.85 (1H, s, H-5); 9.82 (1H, s, OH). ¹³ C NMR δ : 54.1, 54.7, 64.6, 112.3, 120.8, 122.4, 130.2, 133.7, 138.8, 140.0, 154.8, 189.1

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM PERCHLORATES **3**

	M.p., °C	η , %	IR-ATR, cm^{-1}	NMR (DMSO- <i>d</i> 6)
4a	153-154 dec.	100	2989, 1561, 1510, 1470, 1409, 1214, 859, 788	¹ H NMR δ : 3.78 (6H, s, 2CH ₃); 6.92 (1H, m, H-5); 7.01 (1H, m, H-2); 7.08 (1H, d, H-4); 7.34 (1H, dd, H-6); 7.88 (1H, s, H-5). ¹³ C NMR δ : 47.3, 47.7, 112.5, 120.0, 122.6, 130.0, 133.9, 138.8, 139.8, 154.3, 189.0
4b	126-127 dec.	100	3011, 1560, 1457, 1213, 781	¹ H NMR δ : 1.40 (6H, t, 2CH ₃); 3.84 (2H, q, CH ₂ -N); 3.989 (2H, q, CH ₂ -N); 6.93 (1H, m, H-5); 7.03 (1H, m, H-2); 7.08 (1H, m, H-4); 7.32 (1H, m, H-6); 7.92 (1H, s, H-5). ¹³ C NMR δ : 10.6, 53.5, 54.1, 112.2, 120.5, 122.1, 130.3, 1335, 138.7, 140.2, 154.7, 189.8
4c	99-100	100	2966, 1493, 1461, 1273, 840, 774, 620	¹ H NMR δ : 1.78 (6H, m, 3CH ₂); 3.84 (4H, m, 2CH ₂ -N); 6.93 (1H, m, H-5); 7.02 (1H, m, H-2); 7.07 (1H, m, H-4); 7.33 (1H, m, H-6); 7.89 (1H, s, H-5). ¹³ C NMR δ : 21.6, 24.7, 24.9, 56.2, 57.8, 112.5, 120.1, 122.2, 129.3, 133.8, 138.4, 140.3, 154.9, 189.4
4d	87-88 dec.	100	2968, 1543, 1494, 1441, 1339, 1220, 1182, 859, 768	¹ H NMR δ : 3.89 (8H, m, 4CH ₂); 6.93 (1H, m, H-5); 7.02 (1H, d, H-2); 7.08 (1H, m, H-4); 7.33 (1H, m, H-6); 7.83 (1H, s, H-5). ¹³ C NMR δ : 54.0, 54.8, 64.7, 112.4, 120.9, 122.3, 130.1, 133.8, 138.5, 140.3, 154.5, 189.2

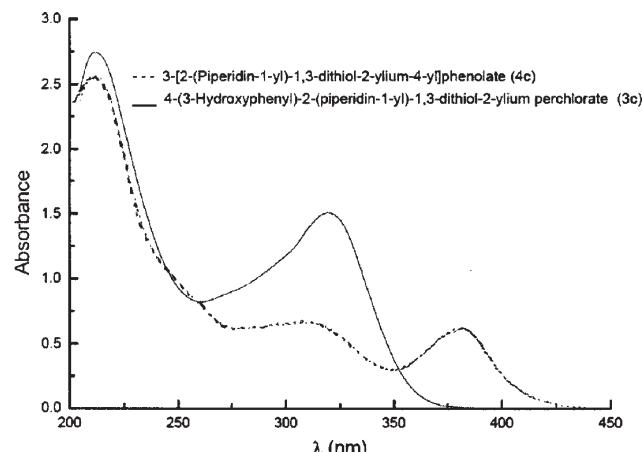


Fig. 1. UV/Vis absorption spectra of 4-(3-hydroxyphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylum perchlorate (**3c**) and 3-[2-(piperidin-1-yl)-1,3-dithiol-2-ylum-4-yl]phenolate (**4c**) in ethanol

methylene hydrogen from compounds **2** (ca. 4.8 ppm) and the appearance of a new signal at a low field (ca. 7.9 ppm) corresponding to the hydrogen atom from the 5-position of the heterocycle. Is worthy to note the high acidity of phenolic hydrogen, with a chemical shift of 9.9 ppm. ¹³C NMR spectra also support the cyclization of dithiocarbamates **2** to the corresponding of 1,3-dithiolium salts by the disappearance of the carbonyl and thiocarbonyl atoms from dithiocarbamates spectra and the appearance of a new signal at a very low field (ca. 189 ppm) which correspond to the electron deficient C-2 atom.

Treatment of perchlorates **3a-d**, under heterogeneous conditions, with saturated aqueous sodium hydrogencarbonate solution affords 3-[2-(dialkylamino)-1,3-dithiol-2-ylum-4-yl]phenolates **4a-d**, in quantitative yields (Scheme 1). The molecular structure of the new compounds was proved by analytical and spectral data (table 3) and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compounds **4** with 70% perchloric acid regenerates the 1,3-dithiolium perchlorates **3** in quantitative yields (Scheme 1).

The presence of a hydroxy substituent in the *ortho*- or *para*-positions induce an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring. In a previous paper [25], the comparative study of UV-Vis absorption spectra of 2-, 3-, and 4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylum-4-yl]phenolates has shown that the yellow color of the above zwitterionic compounds is due to a charge transfer between electron-rich and electron-

deficient regions of the molecules and not to the contribution of quinoid structures in the ground states. The intramolecular nature of the charge-transfer band was proved by measurements at different concentrations. Investigations of UV-Vis absorption spectra of zwitterionic phenolates **4** confirm the previous findings. As shown in figure 1, the absorption band from 375 nm is responsible for the yellow color of phenolates **4**.

Previously place the contribution of a quinoid structure to 2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylum-4-yl]phenolates around 235 nm, partially overlapped by the π - π^* absorption band of aromatic ring. The lack of extended conjugation induces a bathochromic effect for the absorption band of quinoid substructure revealed by an absorption peak at 255 nm.

Conclusions

The synthesis of a new class of zwitterionic 3-[2-(dialkylamino)-1,3-dithiol-2-ylum-4-yl]phenolates has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates. The latter compounds have been synthesized from the reaction of 2-bromo-1-(3-hydroxyphenyl)ethanone with various salts of dithiocarbamic acids. The zwitterionic phenolates exhibit intramolecular charge transfer.

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Table 3
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES **4**

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