A New Class of Mesoionic 4-(1,3-Dithiol-2-ylium)phenolates

RODICA BUHACEANU[1], NECULAI CATALIN LUNGU[1], NORINA CONSUELA FORNA[2], IULIEAN VASILE ASAFTEI[1], PAUL CHIRITA[3], MIHAIL LUCIAN BIRSA[1]*

[1] "Al. I. Cuza" University of Iasi, Department of Chemistry, 11 Carol I Blvd., 700506, Iasi, Romania

[2] University of Medicine and Pharmacy „Gr. T. Popa" Iasi, Department of Removeble Prothesis Oral Implantology and Dental Tehnology, Str. Universitatii 16, 700115, Iasi, Romania

[3] University of Craiova, Department of Chemistry, 107I Calea Bucuresti, 200478, Craiova, Romania

A new class of 4-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates has been synthesized by the heterocondensation of the corresponding phenacyl carbodithioates. The latter compounds have been synthesized following a three step procedure that involves the regioselective bromination of 1-(4-hydroxy-3-methylphenyl)ethanone, followed by the reaction with various salts of dithiocarbamic acids. The mesoionic phenolates exhibit an important bathochromic shift of the charge-transfer absorption band, as compared with the unsubstituted corresponding derivatives.

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

1,3-Dithiolium salts are well-known precursors of tetrathiafulvalenes (TTF) [1-4], which in turn are notable *p*-electron donors in organic metals compounds [5, 6]. TTFs have also recently been studied as donor moieties in intramolecular charge-transfer complexes [7-9]. Although tetrathiafulvalenes are well-known electron donor systems, a variety of acceptor units have been investigated in this context. Special attention has been devoted to cationic systems such as pyridinium and bipyridium cations [10-17]. Of special interest are systems where the donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety [18-22]. In this context, investigations on a series of (1,3-dithiolium-2-yl)phenolates showed that 1,3-dithiolium ions can also serve as an acceptor moiety in intramolecular charge-transfer systems. Recently, we have reported the synthesis of some 4-(hydroxyaryl)-2-(*N*,*N*-dialkylamino)-1,3-dithiolium salts by heterocyclo-functionalization of the corresponding 1-(2-hydroxyaryl)-ethanones and propan-1-ones [23, 24]. To extend the aim of our studies, we report here the synthesis of a new class of mesoionic 4-(1,3-dithiolim-2-yl)phenolates and of the corresponding some 4-(4-hydroxyaryl)-2-(*N*,*N*-dialkyl-amino)-1,3-dithiolium salts.

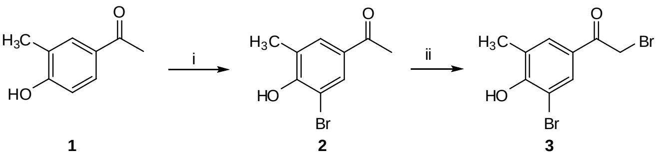
Experimental part

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 (±0.3%) with the calculated values.

Synthesis

1-(4-Hydroxy-3-methylphenyl) ethanone (**1**) has been prepared according to the literature procedure [24], according to figure 1.



i. Br$_2$, 66% AcOH; ii. Br$_2$, glacial AcOH

Fig. 1. Regioselective bromination of 4-hydroxy-3-methylacetophenone

1-(3-Bromo-4-hydroxy-5-methylphenyl)ethanone (**2**)

To a 30g solution of compound (**1**) (0.2 mol) in warm 300 mL aq. AcOH (66%), a 10.3mL solution of bromine (0.2 mol) in 50mL aq. AcOH (66%,) was added dropwise. After complete decoloration the reaction mixture was kept at 4°C for 24h. The precipitate was filtered off, washed with water, dried, and recrystallized from 100mL ethanol. Compound (**2**) was obtained as 38g colorless crystals; yield: 83%; mp 145–146°C. IR (cm^{-1}): 3167, 1648, 1551, 1362, 1309, 1246, 1184, 874, 609. ^{1}H NMR (CDCl$_3$) δ: 2.29 (3H, s, CH$_3$-5); 2.48 (3H, s, CH$_3$-CO); 6.64 (1H, s, OH); 7.71 (1H, d, H-2); 7.91 (1H, d, H-6; J$_{H2-H6}$ = 2.4 Hz).

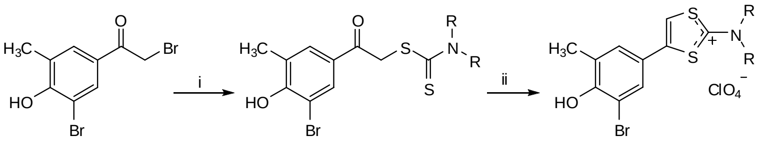
2-Bromo-1-(3-bromo-4-hydroxy-5-methylphenyl) ethanone (**3**)

To a 9.36g solution of (**2**) (43 mmol) in 100 mL warm glacial AcOH, a 2.22mL solution of bromine (43 mmol) in 10mL glacial AcOH was added dropwise at reflux temperature. After complete decoloration, the reaction mixture was cooled to room temperature and then poured into 150mL water. The resultant precipitate was filtered off, washed with water, and dried. Recrystallization from 30mL benzene gave pure (**3**) as 5g colorless crystals; yield: 38%; mp 105-106°C. IR (cm^{-1}): 3148, 1647, 1548, 1442, 1314, 1251, 1188, 1135, 623. ^{1}H NMR (CDCl$_3$) δ: 2.31 (3H, s, CH$_3$-5); 4.33 (2H, s, CH$_2$); 6.27 (1H, s, OH); 7.70 (1H, , H-2); 7.95 (1H, d, H-6; J$_{H2-H6}$=2,3 Hz).

1-(3-Bromo-4-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-piperidine-1-carbodithioate (**4d**)*;* To a 2.5 g solution of 2-bromo-1-(3-bromo-4-hydroxy-5-methylphenyl)ethanone

---

* *email: lbirsa@uaic.ro; Tel: +40 232 201349*



3 **4a-e** **5a-e**

i. $R_2NC(S)S^-$, acetone, reflux; ii. H_2SO_4/AcOH 1:3 (v/v), 80 °C, 70% $HClO_4$

4, 5, 6, 7	R	R
a	CH_3	CH_3
b	CH_2CH_3	CH_2CH_3
c	$(CH_2)_4$	
d	$(CH_2)_5$	
e	$(CH_2)_2$-O-$(CH_2)_2$	

Fig. 2. Synthesis of dithiocarbamates (**4**) and 1,3-dithiolium perchlorates (**5**)

(**3**), (4.8 mmol) in 30 mL acetone, a solution of 1.2g piperidinium piperidine-1-carbodithioate (4.8 mmol) in 20 mL acetone-water (1:1) was added. The reaction mixture was heated at 50°C for 10 min, cooled to room temperature and then poured in water. The precipitate was filtered, washed with water and dried off. Recrystallization from 150mL EtOH, gave 1.6g colorless crystals; yield: 85%. Analytical and spectral data of carbodithioates (**4**) are presented in table 1.

4-(3-Bromo-4-hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**5d**);

To a mixture of 1.2mL sulfuric acid (98%) and 3.6mL glacial acetic acid, 1.2g 1-(3-bromo-4-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-piperidine-1-carbodithioate (**4d**), (3 mmol) was added in small portions. The reaction mixture was heated at 80°C for 10min. After cooling, 0.6mL $HClO_4$ (70%,) and 150mL methyl acetate, were added in this order to isolate the corresponding perchlorate. The precipitate was filtered and dried off. Recrystallization from 60 mL EtOH gave 1.0g colorless crystals; yield: 69%. Analytical and spectral data of 1,3-dithiolium perchlorates (**5**) are presented in table 2.

6-Bromo-1-methyl-4-[2-(piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**6d**)*;*

To a 20mL saturated sodium hydrogencarbonate solution, 1.0g perchlorate (**5d**) (2.12mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2h under vigorous stirring at room temperature, the yellow solid was filtered off, washed with water, and dried. Recrystallization from DMF gave 0.78g yellow crystals; yield: 100%. Analytical and spectral data of 1, 3-dithiolium phenolates (**6**) are presented in table 3.

4-(3-Bromo-4-hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium chloride (**7d**); *General Procedure*

To a suspension of 1g mesoionic phenolate (**6d**) (2.7 mmol) in 10mL acetone, a solution of 1.14mL HCl 37% (13.4 mmol) was added. The reaction mixture was vigorously stirred at rt for 2h, then filtered and washed with acetone. Recrystallization from ethanol gave 1.04g colorless crystals; yield: 95%. Analytical and spectral data of 1,3-dithiolium chlorides (**7**) are presented in table 4.

Table 1

ANALYTICAL AND SPECTRAL DATA OF DITHIOCARBAMATES (**4**)

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
4a	170-171	83	3287, 1686, 1600, 1502, 1478, 1349, 1241, 1102, 967, 847, 647	*^1H NMR* δ : 2.30 (3H, s, CH_3-5); 3.54 (3H, s, CH_3-N); 3.62 (3H, s, CH_3-N); 4.74 (2H, s, CH_2); 7.80 (1H, d, H-2); 8.05 (1H, d, H-6; $J_{H2\text{-}H6}$= 2.0 Hz); 10.10 (1H, s, OH). *^{13}C NMR* δ : 17.6, 41.9, 44.3, 45.8, 111.0, 127.1, 129.5, 130.9, 131.4, 157.0, 190.8, 195.0
4b	157-158	93	3268, 2972, 1663, 1596, 1482, 1412, 1308, 1250, 1085, 912, 661	*^1H NMR* δ : 1.29 (3H, t, CH_3); 1.37 (3H, t, CH_3); 2.31 (3H, s, CH_3-5); 3.84 (2H, q, CH_2); 4.03 (2H, q, CH_2); 4.75 (2H, s, CH_2); 7.81 (1H, d, H-2); 8.05 (1H, d, H-6; $J_{H2\text{-}H6}$= 2,0 Hz); 10.12 (1H, s, OH). *^{13}C NMR* δ : 11.8, 12.9, 17.6, 43.9, 47.3, 50.0, 111.0, 127.1, 129.5, 131.0, 131.5, 157.0, 190.9, 193.8
4c	189-190	88	3294, 2895, 1676, 1597, 1471, 1437, 1308, 1150, 1100, 996, 950, 854, 647	*^1H NMR* δ : 2.09 (2H, m, CH_2); 2.19 (2H, m, CH_2); 2.32 (3H, s, CH_3-5); 3.78 (2H, t, CH_2); 3.90 (2H, t, CH_2); 4.75 (2H, s, CH_2); 7.80 (1H, d, H-2); 8.05 (1H, d, H-6; $J_{H2\text{-}H6}$= 2,1 Hz); 10.08 (1H, s, OH). *^{13}C NMR* δ : 17.8, 24.5, 26.2, 43.7, 51.0, 55.7, 111.2, 127.0, 129.6, 131.2, 131.7, 157.1, 191.1, 193.7
4d	193-194	85	3299, 2929, 1686, 1598, 1492, 1435, 1310, 1237, 1100, 998, 852, 671	*^1H NMR* δ : 1.69 (6H, m, 3CH_2); 2.32 (3H, s, CH_3-5); 3.94 (2H, m, CH_2); 4.23 (2H, m, CH_2); 4.78 (2H, s, CH_2); 7.81 (1H, d, H-2); 8.06 (1H, d, H-6; $J_{H2\text{-}H6}$= 2,1 Hz); 10.02 (1H, s, OH). *^{13}C NMR* δ : 17.1, 23.5, 25.2, 25.8, 43.4, 51.2, 52.8, 110.5, 126.6, 129.1, 130.5, 131.0, 156.6, 190.4, 193.2
4e	201-202	90	3295, 1656, 1593, 1458, 1324, 1262, 1228, 1113, 1032, 991, 657, 538	*^1H NMR* δ : 2.32 (3H, s, CH_3-5); 3.88 (4H, m, CH_2OCH_2); 4.14 (2H, m, CH_2-N); 4.42 (2H, m, CH_2-N); 4.79 (2H, s, CH_2); 7.84 (1H, d, H-2); 8.09 (1H, d, H-6; $J_{H2\text{-}H6}$= 2.1 Hz); 10.12 (1H, s, OH). *^{13}C NMR* δ : 17.4, 43.6, 50.8, 51.5, 65.7, 110.8, 126.4, 128.9, 130.4, 131.2, 156.7, 190.2, 193.3

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM PERCHLORATES (**5**)

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
5a	253-254 dec.	73	3348, 1568, 1534, 1440, 1314, 1192, 1091, 1038, 621	^{1}H *NMR* δ : 2.26 (3H, s, CH_3-5); 3.53 (3H, s, CH_3-N); 3.59 (3H, s, CH_3-N); 7.35 (1H, d, H-2); 7.62 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.6 (1H, s, H-5); 9.71 (1H, s , OH). ^{13}C *NMR* δ : 17.6, 47.4, 47.7, 112.2, 117.1, 122.6, 128.1, 128.7, 128.9, 137.1, 154.3, 185.4
5b	196-197	65	3341, 1563, 1531, 1442, 1302, 1190, 1094, 1043, 620	^{1}H *NMR* δ : 1.41 (3H, t, CH_3); 1.45 (3H, t, CH_3); 2.25 (3H, s, CH_3-5); 3.84 (2H, q, CH_2); 3.95 (2H, q, CH_2); 7.36 (1H, d, H-2); 7.63 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.73 (1H, s, H-5); 9.77 (1H, s, OH). ^{13}C *NMR* δ : 10.8, 17.5, 53.5, 54.5, 112.0, 116.9, 122.8, 128.3, 128.8, 128.9, 137.5, 154.2, 185.9
5c	267-268 dec.	79	3358, 3051, 1578, 1536, 1442, 1195, 1094, 1040, 872, 774, 620	^{1}H *NMR* δ : 2.22 (2H, m, CH_2); 2.25 (3H, s, CH_3-5); 2.28 (2H, m, CH_2); 3.65 (2H, t, CH_2-N); 3.76 (2H, t, CH_2-N); 7.35 (1H, d, H-2); 7.62 (1H, d, H-6; J_{H2-H6}= 2.2 Hz); 7.75 (1H, s, H-5); 9.72 (1H, s, OH). ^{13}C *NMR* δ : 17.4, 26.1, 26.2, 56.4, 56.8, 112.1, 117.0, 122.3, 128.2, 128.6, 128.9, 137.4, 154.1, 185.5
5d	220-221 dec.	69	3347, 3044, 1578, 1538, 1443, 1258, 1097, 1037, 868, 790, 620	^{1}H *NMR* δ : 1.67 (2H, m, CH_2-4); 1.82 (4H, m, CH_2-3 + CH_2-5); 2.25 (3H, s, CH_3-5); 3.81 (2H, m, CH_2-2); 3.86 (2H, m, CH_2-6); 7.37 (1H, d, H-2); 7.64 (1H, d, H-6; J_{H2-H6}= 2.2 Hz); 7.77 (1H, s, H-5); 9.76 (1H, s, OH). ^{13}C *NMR* δ : 17.5, 21.6, 24.89, 24.94, 56.4, 57.7, 112.0, 116.4, 122.8, 128.4, 128.8, 128.9, 136.5, 154.2, 185.8
5e	236-237 dec.	66	3101, 1555, 1526, 1432, 1297, 1110, 1035, 870, 571, 540	^{1}H *NMR* δ : 2.24 (3H, s, CH_3-5); 3.95 (8H, m, 4CH_2); 6.22 (1H, s, OH); 7.35 (1H, d, H-2); 7.61 (1H, d, H-6, J_{H2-H6}= 2.1 Hz); 7.76 (1H, s, H-5). ^{13}C *NMR* δ : 17.3, 54.0, 54.6, 64.5, 112.3, 116.7, 122.9, 128.3, 128.7, 128.9, 136.4, 154.1, 185.7

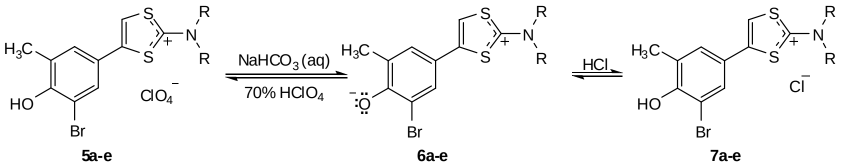


Fig. 3. Synthesis of mesoionic phenolates (**6**) and 1,3-dithiolim chlorides (**7**)

Table 3
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES (**6**)

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
6a	151-152 dec.	100	3198, 1579, 1405, 1335, 1250, 858, 818, 683, 624	^{1}H *NMR* δ : 2.24 (3H, s, CH_3-5); 3.51 (3H, s, CH_3-N); 3.57 (3H, s, CH_3-N); 7.31 (1H, d, H-2); 7.58 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.74 (1H, s, H-5). ^{13}C *NMR* δ : 17.7, 46.8, 47.0, 112.7, 115.1, 120.4, 128.2, 128.5, 128.8, 137.8, 156.8, 185.7
6b	208-209 dec.	100	3080, 1578, 1635, 1444, 1288, 1064, 827, 622	^{1}H *NMR* δ : 1.43 (6H, t, 2CH_3); 2.24 (3H, s, CH_3-5); 3.83 (2H, q, CH_2); 3.91 (2H, q, CH_2); 7.34 (1H, d, H-2); 7.60 (1H, d, H-6; J_{H2-H6}= 2.0 Hz); 7.71 (1H, s, H-5). ^{13}C *NMR* δ : 10.8, 17.8, 53.5, 54.5, 112.8, 115.3, 120.7, 128.3, 128.6, 128.8, 138.0, 156.7, 185.8
6c	214-215 dec.	100	3098, 1573, 1441, 1338, 1255, 816, 748, 620	^{1}H *NMR* δ : 2.22 (4H, m, 2CH_2); 2.24 (3H, s, CH_3-5); 3.63 (2H, t, CH_2-N); 3.72 (2H, t, CH_2-N); 7.33 (1H, d, H-2); 7.60 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.72 (1H, s, H-5). ^{13}C *NMR* δ : 17.7, 26.5, 26.8, 57.1, 57.4, 112.9, 115.4, 120.5, 128.3, 128.5, 128.7, 138.1, 156.5, 185.9
6d	209-210 dec.	100	3077, 2957, 1577, 1535, 1445, 1258, 823, 751, 620	^{1}H *NMR* δ : 1.70 (6H, m, 3CH_2); 2.24 (3H, s, CH_3-5); 3.83 (4H, m, 2CH_2-N); 7.35 (1H, d, H-2); 7.61 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.74 (1H, s, H-5). ^{13}C *NMR* δ : 17.6, 21.6, 24.9, 56.4, 57.6, 112.3, 115.7, 122.0, 128.4, 128.7, 128.8, 136.8, 155.2, 185.8
6e	200-201 dec.	100	2915, 1580, 1473, 1404, 1253, 1189, 864, 824, 624	^{1}H *NMR* δ : 2.24 (3H, s, CH_3-5); 3.98 (8H, m, 4CH_2); 7.35 (1H, d, H-2); 7.60 (1H, d, H-6; J_{H2-H6}= 2.0 Hz); 7.75 (1H, s, H-5). ^{13}C *NMR* δ : 17.8, 53.8, 54.6, 64.8, 112.5, 115.5, 122.3, 128.3, 128.6, 128.8, 136.7, 155.4, 185.7

Table 4
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM CHLORIDES (**7**)

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
7a	247-248 dec.	98	1577, 1475, 1415, 1295, 1187, 622	^{1}H *NMR* δ : 2.26 (3H, s, CH_3-5); 3.53 (3H, s, CH_3-N); 3.58 (3H, s, CH_3-N); 7.35 (1H, d, H-2); 7.64 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.79 (1H, s, H-5); 9.95 (1H, s , OH). ^{13}C *NMR* δ : 17.6, 47.2, 48.2, 112.1, 118.0, 122.8, 128.5, 128.8, 128.9, 137.6, 154.3, 186.7
7b	170-171 dec.	93	1571, 1530, 1442, 1287, 1078, 857, 781, 621	^{1}H *NMR* δ : 1.43 (6H, t, $2CH_3$); 2.25 (3H, s, CH_3-5); 3.85 (2H, q, CH_2); 3.94 (2H, q, CH_2); 7.36 (1H, d, H-2); 7.65 (1H, d, H-6; J_{H2-H6}= 2.2 Hz); 7.76 (1H, s, H-5); 9.97 (1H, s , OH). ^{13}C *NMR* δ : 10.3, 10.7, 17.7, 51.6, 52.8, 112.0, 118.2, 122.5, 128.3, 128.6, 128.8, 137.8, 154.2, 186.9
7c	233-234 dec.	96	1575, 1529, 1442, 1301, 1189, 1036, 874, 620	^{1}H *NMR* δ : 2.22 (4H, m, $2CH_2$); 2.25 (3H, s, CH_3-5); 3.65 (2H, t, CH_2-N); 3.76 (2H, t, CH_2-N); 7.36 (1H, d, H-2); 7.64 (1H, d, H-6; J_{H2-H6}= 2.2 Hz); 7.77 (1H, s, H-5); 9.96 (1H, s , OH). ^{13}C *NMR* δ : 17.5, 26.5, 26.9, 56.7, 57.3, 111.9, 118.1, 122.2, 128.2, 128.5, 128.8, 137.5, 154.2, 186.4
7d	207-208 dec.	95	1578, 1537, 1443, 1257, 1039, 857, 620	^{1}H *NMR* δ : 1.79 (6H, m, $3CH_2$); 2.25 (3H, s, CH_3-5); 3.85 (4H, m, $2CH_2$-N); 7.37 (1H, d, H-2); 7.66 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.78 (1H, s, H-5); 9.96 (1H, s , OH). ^{13}C *NMR* δ : 17.4, 21.5, 24.9, 25.2, 56.3, 57.8, 112.0, 118.4, 122.5, 128.4, 128.7, 130.0, 137.5, 154.2, 186.4
7e	160-161 dec.	95	1568, 1473, 1431, 1256, 1059, 769, 622, 539	^{1}H *NMR* δ : 2.25 (3H, s, CH_3-5); 4.02 (8H, m, $4CH_2$); 7.35 (1H, d, H-2); 7.64 (1H, d, H-6; J_{H2-H6}= 2.1 Hz); 7.77 (1H, s, H-5); 9.96 (1H, s , OH). ^{13}C *NMR* δ : 17.6, 53.4, 54.4, 64.8, 111.8, 117.6, 122.5, 128.2, 128.6, 128.8, 137.4, 154.6, 186.3

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-bromo-4-hydroxy-5-methylphenyl)ethanone (**3**). The required starting materials (**2**) and (**3**) are easily obtained using a regioselective bromination sequence (fig. 1). While 1-(4-hydroxy-3-methylphenyl)ethanone (**1**) has been prepared according to the literature procedure [25], 1-(3-bromo-4-hydroxy-5-methylphenyl)ethanone (**2**) has been synthesized by the selective bromination of the aromatic core in aqueous acetic acid (fig. 1). The reaction of ethanone (**2**) with bromine in glacial acetic acid provided 2-bromo-1-(3-bromo-4-hydroxy-5-methylphenyl)ethanone (**3**) as colorless crystals. The selectivity of the bromination reactions has been supported by the NMR data. Thus, the spectrum of ethanone (**2**) revealed the disappearance of the typical coupling system for a 1,3,4-trisubstituted aromatic ring and the presence of two doublets with a coupling constant corresponding to a reciprocal *meta* orientation (^{4}J = 2.4Hz). The regioselective side-chain bromination was confirmed by the disappearance of the methyl group signal (2.48ppm); a new signal corresponding to two hydrogen atoms appeared at 4.33ppm.

The synthesis of the 1,3-dithiolium ring can be accomplished following two consecutive reactions as described in figure 2. 2-Bromo-1-(3-bromo-4-hydroxy-5-methylphenyl)ethanone (**3**) has been treated with various salts of dialkylaminodithiocarbamic acids in order to provide aminocarbodithioates (**4a-e**), in good isolated yields. The structure of dithiocarbamates (**4**) has been proved by analytical and spectral data (table 1).

Phenacyl carbodithioates are versatile starting materials for the synthesis of various substituted 1,3-dithiolium-2-yl cations under acidic conditions. Using a concentrated sulfuric acid-glacial acetic acid (1:3 v/v) mixture [26, 27] the cyclization of dithiocarbamates (**4a-e**) 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 (**5**) as colorless crystals, in good to excellent yields (table 2). The cyclization of dithiocarbamates (**4**) is accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1660-1686 cm^{-1}) and the presence of a new, strong and broad, absorption band at ca. 1100 cm^{-1}, corresponding to the perchlorate anion. ^{1}H NMR spectra of 1,3-dithiolium-2-yl perchlorates indicate the absence of the methylene hydrogen from compounds (**4**) (ca. 4.7 ppm) and the appearance of a new signal at a low field (ca. 7.7 ppm) corresponding to the hydrogen atom from the 5-position of the heterocycle. ^{13}C NMR spectra also support the cyclization of dithiocarbamates (**4**) 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. 185 ppm) which correspond to the electron deficient C-2 atom.

Treatment of perchlorates (**5a-e**), under heterogeneous conditions, with saturated aqueous sodium hydrogencarbonate solution affords 4-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates (**6a-e**), in quantitative yields (fig. 3). These compounds were isolated as yellow crystalline products that present the features of mesoionic compounds [28, 29]. 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 **6** with 70% perchloric acid regenerates the 1,3-dithiolium perchlorates **5** in quantitative yields (fig. 3).

The presence of a hydroxy substituent in the *para*-position induces an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring (fig. 4). In a previous paper [26], the comparative study of UV-Vis absorption spectra of 2-, 3-, and 4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-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

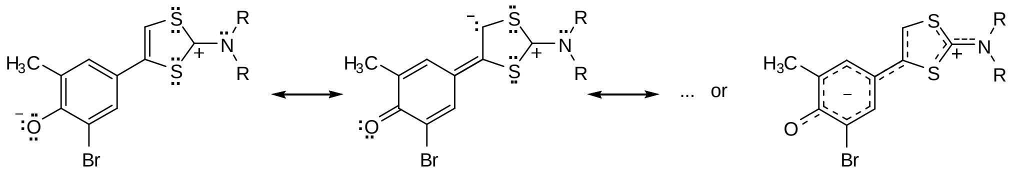


Fig. 4. Extended delocalization charge in mesoionic phenolates (**6**)

intramolecular nature of the charge-transfer band was proved by measurements at different concentrations. Investigations of UV-Vis absorption spectra of mesoionic phenolates (**6**) confirm the previous findings. In comparison to 4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate, the absorption spectra of (**6a-e**) reveal an important bathochromic effect on charge-transfer band. Thus, the position of the charge-transfer absortion band was significantly shifted from 375 nm to more than 400 nm; the most important shift was recorded for (**6a**) (421 nm) and (**6d**) (409 nm). While the intramolecular charge-transfer UV-Vis absorption of such chromophores results from a charge transfer from the HOMO of the donor part to the LUMO of the acceptor part, the electronic effects of the substituents on the extended delocalization of the negative charge should result on a HOMO orbital of lower energy. Moreover, the differences of the position of charge-transfer band between mesoionic phenolates (**6a-e**) also indicate a correlation between dialkylamino substituents and a LUMO orbital of higher energy.

Using the interconversion possibilities between the mesoionic phenolates and its salts, we have been able to isolate the 1,3-dithiolium chlorides (**7a-e**). Thus, 4-(3-bromo-4-hydroxy-5-methylphenyl)-1,3-dithiolium chlorides have been isolated as colorless crystalline products by the treatment of an acetone suspension of mesoionic phenolates (**6**) with 37% hydrochloric acid (fig. 3). The structure of 1,3-dithiolium chlorides was proved by analytical and spectral data (table 4). This class of 1,3-dithiolium salts exhibit a particular interest due to a good solubility in organic solvents and even in water.

Conclusions

The synthesis of a new class of 4-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates. The latter compounds have been synthesized following a three step procedure that involves the regioselective bromination of 1-(4-hydroxy-3-methylphenyl)ethanone, followed by the reaction with various salts of dithiocarbamic acids. The mesoionic phenolates exhibit an important bathochromic shift of the charge-transfer absorption band, as compared with the unsubstituted corresponding derivatives.

Acknowledgments: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project number 51/2012.

References

1.NARITA, M., PITTMAN, C. U. Jr., Synthesis, **1976**, p. 489.
2.SCHUKAT, G., RICHTER, A. M., FANGHANEL, E., Sulfur Rep., **7**, 1987, p. 155.
3.SCHUKAT, G., FANGANEL, E., Sulfur Rep., **14**, 1993, p. 245.
4.SADEKOV, I. D., RIVKIN, B. B., MINKIN, V. I., Sulfur Rep., **15**, 1993, p. 103.
5.YAMADA, J., NISHIKAWA, H., KIKUCHI, K., J. Mater. Chem., **9**, 1999, p. 617.
6.BRYCE, M. R., J. Mater. Chem., **10**, 2000, p. 589.
7.PEREPICHKA, D. F., BRYCE, M. R., BATSANOV, A. S., HOWARD, J. A. K., CUELLO, A. O., GRAY, M., ROTELLO, V. M., J. Org. Chem., **66**, 2001, p. 4517.
8.BRYCE, M. R., GREEN, A., MOORE, A. J., PEREPICHKA, D. F., BATSANOV, A. S., HOWARD, J. A. K., LEDOUX-RAK, I., GONZALES, M., MARTIN, N., SEGURA, J. L., GARIN, J., ORDUNA, J., ALCALA, R., VILLACAMPA, B., Eur. J. Org. Chem., 2001, p. 1927.
9.SANDU, I., GULEA, A., SANDU, I.C.A., LUCA, C., SANDU, I.G., Rev. Chim (Bucharest)., **56**, 8, 2005, p. 805.
10. BACU, E., SAMSON-BELEI, D., NOWOGROCKI, G., COUTURE, A., GRANDCLAUDON, P., Org. Biomol. Chem., **1**, 2003, p. 2377.
11. BELEI, D., DUMEA, C., SAMSON, A., FARCE, A., DUBOIS, J., BICU, E., GHINET, A., Bioorg. Med. Chem. Lett., **22**, 2012, p. 4517.
12. BACIU-ATUDOSIE, L., GHINET, A., BELEI, D., GAUTRET, P., RIGO, B., BICU, E., Tetrahedron Lett., **53**, 2012, p. 6127.
13. BELEI, D., BICU, E., JONES, P. G., BIRSA, M. L., Synlett, **2010**, p. 931.
14. BELEI, D., BICU, E., JONES, P. G., BIRSA, M. L., J. Heterocycl. Chem., **48**, 2011, p. 129.
15. BELEI, D., ABUHAIE, C., BICU, E., JONES, P. G., HOPF, H., BIRSA, M. L., Synlett, **2012**, p. 545.
16. BELEI, D., BICU, E., BIRSA, M. L., Acta Chem. Iasi, **17**, 2009, p. 197.
17. DUMITRIU, G., LUCESCU, L., BICU, E., BELEI, D., Acta Chem. Iasi, **18**, 2010, p. 77.
18. BRYCE, M. R., Adv. Mater., **11**, 1999, p. 11.
19. SUNEL, V., CIUGUREANU, C., BUDEANU, C. H., Rev. Chim. (Bucharest), **37**, 1986, p. 855.
20. CIUGUREANU, C., SUNEL, V., Rev. Chim. (Bucharest), **44**, 1993, p. 875.
21. MOISE, M., SUNEL, V., DULCESCU, M. M., DOROHOI, D. O., Rev. Chim. (Bucharest), **61**,no. 8, 2010, p. 799.
22. CHEPTEA, C., DASCALU, C. F., SUNEL, V., DOROHOI, D. O., Rev. Chim. (Bucharest), **63**, no.3, 2012, p. 319.
23. GOANTA, M., CIOBANU, A.S., BIRSA, A., ASAFTEI, I.V., BIRSA, M. L., Acta Chem. Iasi, **17**, 2009, p. 35.
24. SARBU, L. G., BIRSA, M. L., Acta Chem. Iasi, **19**, 2011, p. 125.
25. CULLINANE, N. M., EDWARDS, B. F. R., J. Chem. Soc., **1958**, p. 2926.
26. BIRSA, M. L., GANJU, D., J. Phys. Org. Chem., **16**, 2003, p. 207.
27. BIRSA, M. L., Sulfur Lett., **26**, 2003, p. 155.
28. SIMAS, A. M., MILLER, J., ATHAYDE FILHO, P. F., Can. J. Chem., **76**, 1998, p. 869.
29. ATHAYDE FILHO, P. F., MILLER, J., SIMAS, A. M., Synthesis, **2000**, p. 1565.

Manuscript received: 4.04.2013