Novel Mesoionic 2-Methyl-4-(1,3-Dithiol-2-ylium)phenolates

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Novel mesoionic 2-methyl-4-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates have been synthesized by the heterocondensation of the 1-(4-hydroxy-3-methylphenyl)-1-oxaethan-2-yl dithiocarbamates. These compounds have been synthesized following a three step procedure that involves the reaction of 2-bromo-1-(4-hydroxy-3-methylphenyl)ethanone with various salts of dithiocarbamic acids, heterocyclocondensation under acidic conditions and treatment with aqueous $NaHCO_3$. The regioselective side-chain bromination of 1-(4-hydroxy-3-methylphenyl)ethanone has been accomplished by an improved experimental procedure.

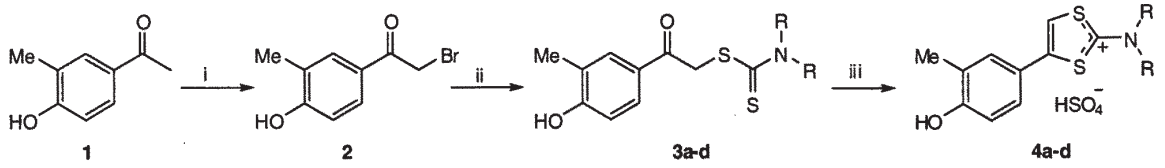
Keywords: dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds, regioselective bromination

Charge transfer salts of tetrathiafulvalenes (TTF) with tetracyanoquinodimethane have attracted widespread interest owing to their quasi-metallic electrical conductivity [1, 2]. 1,3-dithiolium salts are important precursors in the synthesis of tetrathiafulvalenes (TTF) [3-6]. Recent reports highlighted TTFs abilities as donor groups in intramolecular charge-transfer complexes [7, 8]. Concerning acceptor moieties, nitrogen and sulfur containing 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]. Recent studies on (1,3-dithiolium-2-yl)phenolates systems revealed that 1,3-dithiolium cations can act as acceptor groups in intramolecular charge-transfer processes. Following our previous investigation on the synthesis of some 4-(hydroxyaryl)-2-(*N*,*N*-dialkylamino)-1,3-dithiolium salts from the 1-(hydroxyaryl)ethanones and propan-1-ones [22, 23], we wish to extend these studies by presenting a new class of mesoionic 3-methyl-4-(1,3-dithiolim-2-yl)phenolates and the corresponding 4-(3-methyl-4-hydroxyphenyl)-2-(*N*,*N*-dialkylamino)-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 (±0.27%) with the calculated values.



i. Br_2, dioxane; ii. $R_2NC(S)S^-$, acetone, reflux; iii. H_2SO_4/AcOH 1:3 (v/v), 80°C

3, 4, 5, 6	R	R
a	CH_2CH_3	CH_2CH_3
b	$(CH_2)_4$	
c	$(CH_2)_5$	
d	$(CH_2)_2$-O-$(CH_2)_2$	

Scheme 1. Synthesis of dithiocarbamates **3** and 1,3-dithiolium hydrogen sulphates (**4**)

1-(4-Hydroxy-3-methylphenyl)-1-oxaethan-2-yl-pyrrolidine-1-carbodithioate (**3b**)

General Procedure

To a solution of 2-bromo-1-(4-hydroxy-3-methylphenyl) ethanone **2**, (2.29 g, 0.01mol) in acetone (40mL), a solution of pyrrolidinium pyrolidine-1-carbodithioate (2.18 g, 0.01mol) in acetone-water (1:1, 20mL) was added. The reaction mixture was heated at reflux for 15min, cooled to room temperature and then poured in water. The precipitate was filtered, washed with water and dried off. Recrystallization from EtOH (50mL) gave colorless crystals; yield 2.44g (83%). Analytical and spectral data of carbodithioates **3** are presented in table 1.

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	M.p., (°C)	η, (%)	IR-ATR, (cm^{-1})	NMR ($CDCl_3$)
3a	159 - 160	82	3281, 1682, 1601, 1582, 1475, 1351, 1239, 1100, 962, 843	*^1H NMR* δ : 1.19 (3H, t, CH_3); 1.23 (3H, t, CH_3); 2.23 (3H, s, CH_3); 3.81 (2H, q, CH_2); 3.95 (2H, q, CH_2); 4.83 (2H, s, CH_2); 6.80 (1H, d, H-5); 7.29 (1H, dd, H-6; J_{H5-H6}= 9.0 Hz); 7.69 (1H, d, H-2, J_{H2-H6}= 2.3 Hz); 11.57 (1H, s, OH). *^{13}C NMR* δ : 11.8, 12.8, 17.5, 43.9, 47.4, 50.1, 119.0, 127.1, 129.6, 131.0, 131.2, 157.1, 190.9, 193.8
3b	181 - 182	83	3290, 2899, 1678, 1595, 1473, 1299, 1155, 1107, 988, 952, 850	*^1H NMR* δ : 1.47 (2H, m, CH_2); 1.59 (2H, m, CH_2); 1.81 (3H, s, CH_3-5); 3.24 (2H, t, CH_2); 3.40 (2H, t, CH_2); 4.93 (2H, s, CH_2); 6.37 (1H, d, H-5); 6.80 (1H, dd, H-6; J_{H5-H6}= 9.4 Hz); 7.24 (1H, d, H-2, J_{H2-H6}= 2.5 Hz); 11.15 (1H, s, OH). *^{13}C NMR* δ : 17.9, 24.5, 26.3, 43.8, 51.1, 55.6, 119.1, 127.0, 129.5, 131.1, 131.7, 157.5, 191.2, 193.7
3c	189 - 190	82	3295, 2921, 1680, 1595, 1488, 1437, 1308, 1235, 1102, 991, 847	*^1H NMR* δ : 1.70 (6 H, m, $3CH_2$); 2.29 (3H, s, CH_3-5); 4.13 (4H, m, $2CH_2$); 4.92 (2H, s, CH_2); 6.88 (1H, d, H-5); 7.32 (1H, dd, H-6; J_{H5-H6}= 9.1 Hz); 7.75 (1H, d, H-2, J_{H2-H6}= 2.4 Hz); 11.62 (1H, s, OH). *^{13}C NMR* δ : 17.2, 23.5, 25.4, 25.8, 43.5, 51.2, 52.9, 119.5, 126.7, 129.1, 130.7, 131.5, 156.7, 190.5, 193.2
3d	192 - 193	79	3299, 1677, 1591, 1452, 1323, 1258, 1219, 1107, 1031, 995	*^1H NMR* δ : 2.29 (3H, s, CH_3-5); 3.75 (4H, m, CH_2-O-CH_2); 4.12 (4H, m, CH_2-N-CH_2); 4.97 (2H, s, CH_2); 6.83 (1H, d, H-5); 7.32 (1H, dd, H-6; J_{H5-H6}=10.1 Hz); 7.77 (1H, d, H-2, J_{H2-H6}= 2.3 Hz); 11.34 (1H, s, OH). *^{13}C NMR* δ : 17.3, 43.6, 50.9, 51.6, 65.6, 119.8, 126.5, 128.8, 130.5, 131.3, 156.7, 190.3, 193.3

Table 1
ANALYTICAL AND SPECTRAL DATA OF DITHIOCARBAMATES **3**

	M.p., (°C)	η, (%)	IR-ATR, (cm^{-1})	NMR (DMSO-*d6*)
4a	179-180	81	3022, 1561, 1488, 1401, 1295, 1114, 831	*^1H NMR* δ : 1.36 (6H, t, $2CH_3$); 2.16 (3H, s, CH_3-3); 3.80 (2H, q, CH_2); 3.91 (2H, q, CH_2); 6.85 (1H, d, H-5); 7.26 (1H, dd, H-6; $J_{H5-H6'}$= 7.0 Hz); 7.34 (1H, d, H-2; $J_{H2-H6'}$=2.1 Hz); 7.74 (1H, s, H-5); 9.19 (2H, s, HSO_4 + OH). *^{13}C NMR* δ : 10.7, 17.6, 53.5, 54.4, 116.0, 119.9, 122.7, 128.3, 128.8, 128.9, 137.6, 154.2, 185.9
4b	195-196	90	2994, 1555, 1475, 1405, 1222, 1148, 1032, 847	*^1H NMR* δ : 2.15 (3H, s, CH_3-3); 2.23 (4H, m, $2CH_2$); 3.74 (4H, m, $2CH_2$); 6.87 (1H, d, H-5); 7.28 (1H, dd, H-6; J_{H5-H6}= 7.9 Hz); 7.35 (1H, d, H-2; $J_{H2-H6'}$=2.1 Hz); 7.75 (1H, s, H-5); 9.54 (2H, s, HSO_4 + OH). *^{13}C NMR* δ : 17.5, 26.1, 26.3, 56.4, 56.8, 116.1, 119.0, 122.3, 128.1, 128.5, 128.9, 137.4, 154.1, 185.4
4c	212 - 213	88	2984, 1560, 1444, 1402, 1219, 1150, 1045, 859	*^1H NMR* δ : 1.76 (6H, m, $3CH_2$); 2.13 (3H, s, CH_3-5); 3.86 (4H, m, $2CH_2$); 6.90 (1H, d, H-5); 7.24 (1H, dd, H-6; J_{H5-H6}= 7.7 Hz); 7.30 (1H, d, H-2; J_{H2-H6}=2.0 Hz); 7.72 (1H, s, H-5); 9.13 (2H, s, HSO_4 + OH). *^{13}C NMR* δ : 17.6, 21.6, 24.8, 24.9, 56.5, 57.7, 116.0, 119.4, 122.9, 128.5, 128.7, 128.9, 136.8, 154.2, 185.7
4d	210-211	86	2982, 1558, 1456, 1408, 1236, 1144, 1041, 849	*^1H NMR* δ : 2.14 (3H, s, CH_3-5); 3.90 (8H, m, $4CH_2$); 6.92 (1H, d, H-5); 7.29 (1H, dd, H-6; J_{H5-H6}= 8.0 Hz); 7.33 (1H, d, H-2; J_{H2-H6}=2.0 Hz); 7.76 (1H, s, H-5); 9.75 (2H, s, HSO_4 + OH). *^{13}C NMR* δ : 17.4, 54.1, 54.6, 64.4, 116.1, 119.5, 122.7, 128.1, 128.6, 128.9, 136.4, 154.1, 185.4

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM HYDROGEN SULPHATES **4**

4-(4-Hydroxy-3-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium hydrogen sulphate (**4b**)

General Procedure

To a mixture of sulfuric acid (98%, 1.0mL) and glacial acetic acid (3.0mL), 1-(4-hydroxy-3-methylphenyl)-1-oxaethan-2-yl-pyrrolidine-1-carbodithioate **3b**, (1.0g, 3.38mmol) was added in small portions. The reaction mixture was heated at 80°C for 10 min. After cooling, water was added and the precipitate was filtered and dried off. Recrystallization from EtOH (100mL) gave colorless crystals; yield 1.14g (90%). Analytical and spectral data of 1,3-dithiolium hydrogen sulphates **3** are presented in table 2.

2-Methyl-4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]-phenolate (**5b**)

General Procedure

To a saturated sodium hydrogen carbonate solution (20-mL), hydrogen sulphate **4b** (1.0g, 2.66mmol) 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 dichloromethane gave yellow crystals; yield 0.74g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **5** are presented in table 3.

4-(4-Hydroxy-3-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**6b**)

General Procedure

To a suspension of mesoionic phenolate **5b** (1.0g, 3.6mmol) in 10mL acetone a solution of 1.0mL 70% $HClO_4$ was added. The reaction mixture was vigorously stirred at rt for 2h, then filtered and washed with acetone. Recrystallization from EtOH (70mL) gave colorless crystals; yield 1.36g (100%). Analytical and spectral data of 1,3-dithiolium perchlorates **6** are presented in table 4.

Results and discussions

The synthetic strategy for the target compounds involves two major steps: the synthesis of the 1,3-dithiolium ring, followed by the exploitation of interconversion properties of the corresponding mesoionic 1,3-dithiolium phenolates. The first step can be accomplished following three

	M.p., (°C)	η, (%)	IR-ATR, (cm^{-1})	NMR (DMSO-*d6*)
5a	165-166 dec.	100	3128, 1577, 1401, 1339, 1249, 848, 811, 781	*^1H NMR* δ : 1.35 (6H, t, $2CH_3$); 2.14 (3H, s, CH_3-2); 3.80 (2H, q, CH_2); 3.85 (2H, q, CH_2); 6.85 (1H, d, H-6); 7.26 (1H, dd, H-5; J_{H5-H6}= 6.5 Hz); 7.31 (1H, d, H-3; J_{H3-H5}=2.1 Hz); 7.61 (1H, s, H-5). *^{13}C NMR* δ : 10.9, 17.4, 53.7, 54.5, 115.8, 119.3, 120.7, 128.3, 128.6, 128.8, 138.1, 156.7, 185.4
5b	143-144 dec.	100	3099, 1574, 1422, 1335, 1251, 814, 752	*^1H NMR* δ : 2.15 (3H, s, CH_3-2); 2.21 (4H, m, $2CH_2$); 3.73 (4H, m, $2CH_2$); 6.86 (1H, d, H-6); 7.28 (1H, dd, H-5; J_{H5-H6}= 8.0 Hz); 7.32 (1H, d, H-3; J_{H3-H5}=2.1 Hz); 7.61 (1H, s, H-5). *^{13}C NMR* δ : 17.5, 26.6, 26.8, 57.1, 57.3, 115.8, 119.3, 120.4, 128.3, 128.5, 128.7, 138.1, 156.5, 185.7
5c	127-128 dec.	100	3079, 1575, 1441, 1252, 828, 759	*^1H NMR* δ : 1.74 (6H, m, $3CH_2$); 2.14 (3H, s, CH_3-2); 3.88 (4H, m, $2CH_2$); 6.87 (1H, d, H-6); 7.30 (1H, dd, H-5; J_{H5-H6}= 7.8 Hz); 7.34 (1H, d, H-3; J_{H3-H5}=2.0 Hz); 7.62 (1H, s, H-5). *^{13}C NMR* δ : 17.6, 21.5, 24.9, 56.3, 57.6, 115.3, 119.7, 122.0, 128.4, 128.6, 128.8, 136.9, 155.2, 185.2
5d	105-106 dec.	100	29199, 1578, 1444, 1401, 1250, 1180, 857, 827	*^1H NMR* δ : 2.14 (3H, s, CH_3-2); 3.90 (8H, m, $4CH_2$); 6.89 (1H, d, H-6); 7.30 (1H, dd, H-5; J_{H5-H6}= 7.6 Hz); 7.32 (1H, d, H-3; J_{H3-H5}=2.0 Hz); 7.32 (1H, s, H-5). *^{13}C NMR* δ : 17.7, 53.7, 54.7, 64.8, 115.5, 119.5, 122.3, 128.3, 128.6, 128.8, 136.7, 155.5, 185.9

Table 3
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES **5**

	M.p., (°C)	η, (%)	IR-ATR, (cm^{-1})	NMR (DMSO-*d6*)
6a	191-192	100	3351, 1562, 1535, 1444, 1310, 1197, 1090, 1032, 778	*^1H NMR* δ : 1.38 (6H, t, $2CH_3$); 2.17 (3H, s, CH_3-3); 3.82 (2H, q, CH_2); 3.93 (2H, q, CH_2); 6.87 (1H, d, H-5); 7.28 (1H, dd, H-6; J_{H5-H6}= 6.9 Hz); 7.34 (1H, d, H-2; J_{H2-H6}=2.1 Hz); 7.64 (1H, s, H-5); 9.92 (1H, s, OH). *^{13}C NMR* δ : 10.8, 17.7, 53.5, 54.4, 116.1, 119.8, 122.7, 128.3, 128.7, 128.9, 137.6, 154.2, 185.8
6b	258 - 259 dec.	100	3355, 3049, 1572, 1531, 1443, 1191, 1095, 1041, 774	*^1H NMR* δ : 2.15 (3H, s, CH_3-3); 2.22 (4H, m, $2CH_2$); 3.74 (4H, m, $2CH_2$); 6.88 (1H, d, H-5); 7.30 (1H, dd, H-6; J_{H5-H6}= 8.6 Hz); 7.36 (1H, d, H-2; J_{H2-H6}=2.1 Hz); 7.64 (1H, s, H-5); 10.03 (1H, s, OH). *^{13}C NMR* δ : 17.6, 26.0, 26.3, 56.3, 56.9, 116.2, 119.1, 122.3, 128.1, 128.6, 128.9, 137.5, 154.1, 185.3
6c	234 - 235	100	3349, 3041, 1572, 1535, 1441, 1253, 1089, 1039, 788	*^1H NMR* δ : 1.76 (6H, m, $3CH_2$); 2.16 (3H, s, CH_3-5); 3.89 (4H, m, $2CH_2$); 6.89 (1H, d, H-5); 7.32 (1H, dd, H-6; J_{H5-H6}= 7.9 Hz); 7.36 (1H, d, H-2; J_{H2-H6}=2.0 Hz); 7.65 (1H, s, H-5); 9.93 (1H, s, OH). *^{13}C NMR* δ : 17.5, 21.5, 24.8, 24.9, 56.5, 57.8, 116.3, 119.7, 122.8, 128.5, 128.8, 128.9, 136.8, 154.3, 185.4
6d	241 - 242	100	3341, 1559, 1532, 1438, 1292, 1102, 1034, 777	*^1H NMR* δ : 2.15 (3H, s, CH_3-5); 3.92 (8H, m, $4CH_2$); 6.90 (1H, d, H-5); 7.31 (1H, dd, H-6; J_{H5-H6}= 8.0 Hz); 7.33 (1H, d, H-2; J_{H2-H6}=2.0 Hz); 7.36 (1H, s, H-5); 9.95 (1H, s, OH). *^{13}C NMR* δ : 17.3, 54.1, 54.7, 64.4, 116.2, 119.8, 122.9, 128.2, 128.5, 128.9, 136.5, 154.2, 185.7

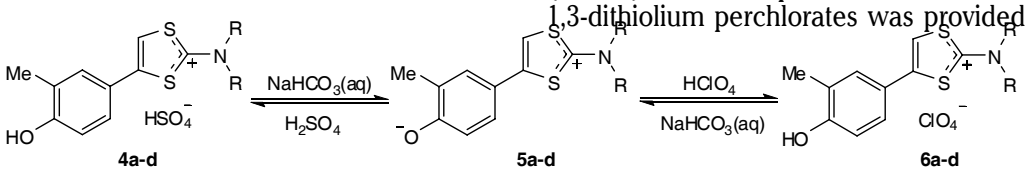
Table 4
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM PERCHLORATES **6**

consecutive reactions as described in scheme 1. A literature survey indicated several method for the synthesis of 2-bromo-1-(4-hydroxy-3-methylphenyl)ethanone (**2**). However, most of the procedures lead to mixtures of side-chain and aromatic core bromination products. A particular method, consisting in regioselective side-chain bromination of substituted acetophenones with the molecular bromine-dioxane complex was found of interest [24]. Although this molecular complex has been used as mild and selective bromination reagent [25], there are important isolation and handling issues; it must be kept under 0°C and easily lose molecular bromine [26]. In order to avoid the above mentioned difficulties we followed an improved experimental procedure by using in situ generated molecular bromine-dioxane complex. Thus, one equivalent of bromine was mixed with one equivalent of dioxane; then anhydrous dioxane was added until all solid particles of bromine-dioxane complex was dissolved. This solution was added dropwise to a solution of 1-(4-hydroxy-3-methylphenyl)ethanone (**1**) [27] in anhydrous dioxane at room temperature, following the complete discoloration of the reaction mixture. 2-Bromo-1-(4-hydroxy-3-methylphenyl)ethanone (**2**) has been treated with various salts of dialkylaminodithiocarbamic acids in order to provide aminocarbodithioates **3a-d**, in good isolated yields (scheme 1). The structure of dithiocarbamates **3** has been proved by analytical and spectral data (table 1).

Phenacyl carbodithioates are important precursors of various substituted 1,3-dithiol-2-ylium cations. Using a concentrated sulfuric acid-glacial acetic acid (1:3 v/v) mixture [28, 29] the cyclization of dithiocarbamates **3a-d** takes place under mild reaction conditions. After 10 min at 80°C the homogeneous reaction mixture was cooled to room temperature and poured into water. Filtration and recrystallization of the precipitate gives hydrogen sulphates as colorless crystals, in good to excellent yields (table 2). The cyclization of dithiocarbamates **3** was accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1670cm^{-1}) and the presence of a new, strong and broad absorption band at ca. 1100cm^{-1}, corresponding to the hydrogen sulfate anion.

The NMR spectra also confirm the heterocyclization of dithiocarbamates **3**. Thus, the ^1H NMR spectra of 1,3-dithiol-2-ylium hydrogen sulphates indicate the absence of the methylene hydrogens from compounds **3** (ca. 4.9ppm) and appearance of a new signal at a low field (ca. 7.6ppm) corresponding to the hydrogen atom from the 5-position of the heterocycle. ^{13}C NMR spectra also support the synthesis of 1,3-dithiolium salts **4** by the disappearance of the carbonyl and thiocarbonyl carbon atoms present in the dithiocarbamates spectra and the appearance of a new signal at a very low field (ca. 185ppm) which correspond to the electron deficient C-2 atom.

Treatment of hydrogen sulphates **4a-d**, under heterogeneous conditions, with saturated aqueous sodium hydrogen carbonate solution affords 2-methyl-4-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **5a-d**, in quantitative yields as yellow compounds (scheme 2). 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 **5** with conc. sulfuric acid regenerates the 1,3-dithiolium sulphates **4** in quantitative yields (scheme 2). Moreover, by treating a slurry of **5** in acetone with 70% perchloric acid 1,3-dithiolium perchlorates **6a-d** were obtained in quantitative yields (scheme 2). The molecular structure of the new perchlorates was proved by analytical and spectral data (table 4). The main spectral indication for the synthesis of 1,3-dithiolium perchlorates was provided by IR spectra



Scheme 2.Interconversion of 1,3-dithiolium salts **4** and **6** with corresponding mesoionic phenolates

were broad and strong absorption bands of perchlorate anion are present at 1100-1200cm^{-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 [28], 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 these 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 yellow color of mesoionic phenolates 5a-d is also provided by an intramolecular charge transfer. The intramolecular nature of the charge-transfer band was again proved by measurements at different concentrations.

Conclusions

The synthesis of novel mesoionic 2-methyl-4-[2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates. These compounds have been synthesized from the reaction of 2-bromo-1-(4-hydroxy-3-methylphenyl)ethanone with various salts of dithiocarbamic acids. An improved experimental procedure for the regioselective side-chain bromination of 1-(4-hydroxy-3-methylphenyl)ethanone is reported.

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

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Manuscript received: 13.08.2013