# 5-Methyl-4-(5-Bromo-2-hydroxyphenyl)-1,3-Dithiolium Derivatives

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*Novel 4-(5-bromo-2-hydroxyphenyl)-5-methyl-2-(N,N-dialkylamino)-1,3-dithiol-2-ylium hydrogen sulphates have been synthesized by the heterocyclisation of the 1-(5-bromo-2-hydroxyphenyl)-1-oxapropan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the corresponding substituted a-bromopropiophenone with various salts of dithiocarbamic acids. These derivatives were characterized by NMR and MS spectrometry, UV-Vis and IR spectroscopy.*

*Keywords: dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds, propiophenones*

The discovery of highly conductive organic charge transfer complexes tetrathiafulvalenes derivatives (TTF) with tetracyano-*p*-quinodimethane [1, 2] has prompted interest in the synthesis of new 1,3-dithiolium salts which are well-known precursors of TTFs [3-6]. Recent reports highlighted the TTFs ability to act as donor groups in intramolecular charge-transfer complexes [7, 8]. In this context, a variety of acceptor units have been investigated, nitrogen and sulfur containing cations receiving a great deal of attention [9-19]. Of special interest for conducting materials are charge-transfer [20-30] and push-pull [31-47] compounds. 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 [27, 30, 48, 49]. 1,3-Dithiolium systems are known for their reactivity at the C(2)-position towards nucleophiles [28]. Moreover, this type of compounds has been found to exhibit biological activity, in a particular case, against gram-positive and gram-negative bacteria [50-60].

We are reporting here the synthesis of novel 4-(5-bromo-2-hydroxyphenyl)-5-methyl-2-(*N,N*-dialkylamino)-1,3-dithiolium salts and the corresponding mesoionic 4-bromo-2-(5-methyl-1,3-dithiolim-2-yl)phenolates.

## Experimental part

### *Analysis methods*

Melting points were obtained on a KSPI melting point apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from TMS. UV-Vis spectra were recorded on a Varian BioChem 100 spectrophotometer. Mass spectra were recorded on a Thermo Scientific ISQ LT instrument. Elemental analyses (C, H, N and S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.28%) with the calculated values.

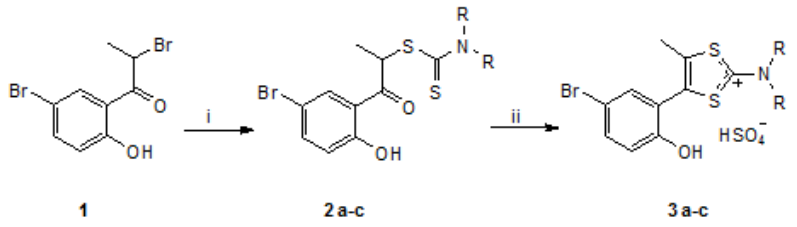
### *Synthesis*

The synthetic pathway for the synthesis of dithiocarbamates **2a-c** and 1,3-dithiolium hydrogen sulphates **3a-c** is described in scheme 1.

*1-(5-Bromo-2-hydroxyphenyl)-1-oxopropan-2-yl-N,N-dimethyldithiocarbamate* (**2a**)*;*

General Procedure

To a solution of 2-bromo-1-(5-bromo-2-hydroxyphenyl)propan-1-one (**1**, 3.08g, 0.01mol) in acetone (30mL), a solution of *N,N*-dimethylammonium *N,N*-dimethyldithiocarbamate (1.66g, 0.01mol) in acetone-water (1:1, 20mL) was added. The reaction mixture was refluxed for 10 min, cooled to room temperature and then poured in water. The precipitate was filtered, washed with water and dried off. Recrystallization from *i*-PrOH (30mL) gave colorless crystals; yield 2.9 g (85%). Analytical and spectral data of carbodithioates **2a-c** are presented in table 1.




1 2a-c 3a-c

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

Scheme 1. Synthesis of dithiocarbamates **2** and 1,3-dithiolium hydrogen sulphates **3**

| 2, 3, 4 | R | R |
|---|---|---|
| a | $-CH_3$ | $-CH_3$ |
| b | $-CH_2CH_3$ | $-CH_2CH_3$ |
| c | $-(CH_2)_5-$ | |

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**Table 1**

ANALYTICAL AND SPECTRAL DATA OF DITHIOCARBAMATES **2**

| | M.p., °C | η, % | IR-ATR, $cm^{-1}$ | NMR ($CDCl_3$) |
|---|---|---|---|---|
| **2a** | 130 - 131 | 85 | 2982, 1642, 1435, 1318, 1252, 1211, 1138, 851, 783, 668 | *$^1H$ NMR* δ : 1.54 (3H, d, $CH_3$); 3.48 (6H, s, $2CH_3$); 5.74 (1H, q, CH); 6.87 (1H, d, H-3); 7.49 (1H, dd, H-4; $J_{H3-H4}$=8.2 Hz); 8.12 (1H, d, H-6, $J_{H4-H6}$=1.4 Hz); 11.75 (1H, s, OH) ppm. *$^{13}C$ NMR* δ : 17.4, 41.5, 45.9, 51.4, 111.4, 119.9, 120.8, 133.5, 161.8, 192.7, 203.2 ppm. |
| **2b** | 92 - 93 | 86 | 2984, 2915, 1648, 1499, 1280, 1198, 984, 840, 635 | *$^1H$ NMR* δ : 1.26 (6H, t, $2CH_3$); 1.58 (3H, d, $CH_3$); 3.81 (4H, m, $2CH_2$); 5.75 (1H, q, CH); 6.84 (1H, d, H-3); 7.48 (1H, dd, H-4; $J_{H3-H4}$=9.0 Hz); 8.11 (1H, d, H-6, $J_{H4-H6}$=1.3 Hz); 11.90 (1H, s, OH) ppm. *$^{13}C$ NMR* δ : 12.1, 13.2, 17.2, 47.9, 50.9, 51.4, 111.1, 119.5, 121.0, 133.3, 162.1, 192.9, 203.1 ppm. |
| **2c** | 103-104 | 84 | 2972, 1647, 1439, 1322, 1248, 1218, 1135, 850, 785, 680 | *$^1H$ NMR* δ : 1.56 (3H, d, $CH_3$); 1.75 (6H, m, $3CH_2$); 4.10 (4H, m, $2CH_2$-N); 5.76 (1H, q, CH); 6.86 (1H, d, H-3); 7.53 (1H, dd, H-4; $J_{H3-H4}$=7.9 Hz); 8.09 (1H, d, H-6, $J_{H4-H6}$=1.2 Hz); 11.68 (1H, s, OH) ppm. *$^{13}C$ NMR* δ : 17.5, 24.7, 26.1, 26.7, 51.5, 52.4, 54.3, 111.3, 119.8, 121.1, 133.1, 162.4, 192.8, 203.5 ppm. |

**Table 2**

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

| | M.p., °C | η, % | IR-ATR, $cm^{-1}$ | NMR (DMSO-*d6*) |
|---|---|---|---|---|
| **3a** | 244-245 dec. | 81 | 3051, 2978, 1556, 1438, 1102, 1011, 860, 778, 570 | *$^1H$ NMR* δ : 2.27 (3H, s, $CH_3$-5); 3.58 (3H, s, $CH_3$-N); 3.61 (3H, s, $CH_3$-N); 5.28 (2H, s, OH + $HSO_4$); 6.98 (1H, d, H-3); 7.51 (1H, d, H-6); 7.54 (1H, dd, H-4; $J_{H3-H4}$=9.4 Hz; $J_{H4-H6}$=2.0 Hz) ppm. *$^{13}C$ NMR* δ : 14.6, 47.1, 46.7, 110.6, 116.9, 118.1, 126.0, 131.7, 133.0, 134.2, 155.4, 183.1 ppm. |
| **3b** | 280-281 dec. | 68 | 3049, 2984, 1548, 1431, 1108, 854, 765, 569 | *$^1H$ NMR* δ : 1.44 (6H, t, $2CH_3$); 2.29 (3H, s, $CH_3$-5); 3.90 (2H, q, $CH_2$); 3.94 (2H, q, $CH_2$); 5.30 (2H, s, OH + $HSO_4$); 7.00 (1H, d, H-3); 7.53 (1H, d, H-6); 7.56 (1H, dd, H-4; $J_{H3-H4}$=9.2 Hz; $J_{H4-H6}$=2.1 Hz) ppm. *$^{13}C$ NMR* δ : 14.5, 17.0, 53.2, 54.2, 110.5, 117.1, 118.4, 126.2, 131.8, 133.1, 134.4, 155.0, 183.3 ppm. |
| **3c** | 204-205 | 86 | 3054, 1555, 1424, 1251, 1068, 874, 615, 553 | *$^1H$ NMR* δ : 1.80 (6H, m, $3CH_2$); 2.23 (3H, s, $CH_3$-5); 3.86 (4H, m, $2CH_2$); 5.41 (2H, s, OH + $HSO_4$); 7.05 (1H, d, H-3); 7.52 (1H, d, H-6); 7.55 (1H, dd, H-4; $J_{H3-H4}$=9.1 Hz; $J_{H4-H6}$=2.1 Hz) ppm. *$^{13}C$ NMR* δ : 14.8, 21.1, 24.4, 56.1, 110.1, 117.3, 118.5, 126.3, 131.6, 133.3, 134.5, 155.0, 183.5 ppm. |

*4-(5-Bromo-2-hydroxyphenyl)-5-methyl-2-(N,N-dimethylamino)-1,3-dithiol-2-ylium hydrogen sulphate* (**3a**)

General Procedure

To a mixture of sulfuric acid (98%, 2mL) and glacial acetic acid (6mL), 1-(5-bromo-2-hydroxyphenyl)-1-oxopropan-2-yl-*N,N*-dimethyldithiocarbamate (**2a**, 2g, 5.7mmol) was added in small portions. The reaction mixture was heated at 80 °C for 10 min. After cooling, water (100mL) was added and the precipitate was filtered and dried off. Recrystallization from EtOH (75mL) gave colorless crystals; yield 2g (81%). Analytical and spectral data of 1,3-dithiolium hydrogen sulphates **3a-c** are presented in table 2.

*4-Bromo-2-[5-methyl-2-(N,N-dimethylamino)-1,3-dithiol-2-ylium-4-yl]phenolate (4a);*

General Procedure

To a saturated sodium hydrogen carbonate solution (20mL), hydrogen sulphate **3a** (1g, 2.3 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 *N,N*-dimethylformamide gave yellow crystals; yield 0.77g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **4a-c** are presented in table 3.

**Table 3**

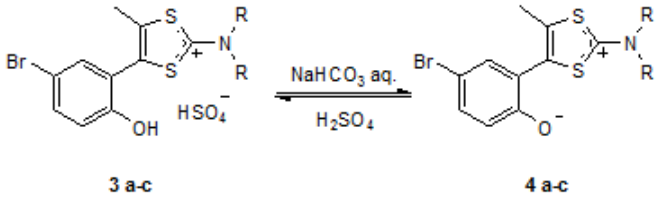
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES **4**

| | M.p., °C | η, % | IR-ATR, $cm^{-1}$ | NMR (DMSO-*d6*) |
|---|---|---|---|---|
| **4a** | 226-227 dec. | 100 | 2968, 1544, 1499, 1452, 1263, 1214, 1133, 854, 712, 660 | *$^1H$ NMR* δ : 2.32 (3H, s, $CH_3$-5); 3.53 (3H, s, $CH_3$-N); 3.55 (3H, s, $CH_3$-N); 6.97 (1H, d, H-3); 7.49 (1H, d, H-6); 7.52 (1H, dd, H-4; $J_{H3-H4}$=8.9 Hz; $J_{H4-H6}$=2.3 Hz) ppm. *$^{13}C$ NMR* δ : 14.5, 47.0, 46.5, 110.4, 116.8, 118.0, 125.7, 131.5, 133.3, 134.1, 155.4, 183.5 ppm. |
| **4b** | 247-248 dec. | 100 | 2954, 1548, 1491, 1448, 1254, 1208, 1128, 850, 725, 651 | *$^1H$ NMR* δ : 1.37 (3H, t, $CH_3$); 1.40 (3H, t, $CH_3$); 2.31 (3H, s, $CH_3$-5); 3.85 (4H, q, $2CH_2$); 6.96 (1H, d, H-3); 7,50 (1H, d, H-6); 7.52 (1H, dd, H-4; $J_{H3-H4}$=8.8 Hz; $J_{H4-H6}$=2.3 Hz) ppm. *$^{13}C$ NMR* δ : 14.5, 16.8, 53.1, 54.2, 110.6, 117.0, 118.1, 126.5, 131.7, 133.1, 134.4, 155.1, 183.1 ppm. |
| **4c** | 210-211 dec. | 100 | 2944, 1550, 1498, 1445, 1248, 1135, 848, 711, 660 | *$^1H$ NMR* δ : 1.78 (6H, m, $3CH_2$); 2.31 (3H, s, $CH_3$-5); 3.84 (4H, m, $2CH_2$); 7.00 (1H, d, H-3); 7.50 (1H, d, H-6); 7.53 (1H, dd, H-4; $J_{H3-H4}$=8.7 Hz; $J_{H4-H6}$=2.3 Hz) ppm. *$^{13}C$ NMR* δ : 14.7, 21.1, 24.5, 56.0, 110.4, 117.1, 118.3, 126.5, 131.6, 133.2, 134.5, 154.8, 184.2 ppm. |

## 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 [23-26, 61]. The reactions of *a*-bromophenones with salts of dithiocarbamic acid, readily available from the reaction of secondary amine with carbon disulfide [62], represent an accessible way to various substituted phenacyl carbodithioates. The synthesis of the 1,3-dithiolium ring can be accomplished following two consecutive reactions as described in scheme 1. In a first step, phenacyl dithiocarbamates **2a-c** were obtained by reacting 2-bromo-1-(5-bromo-2-hydroxyphenyl)propan-1-one (**1**) [63, 64] with *N,N*-dimethylammonium *N,N*-dimethyldithiocarbamate, sodium *N,N*-diethyldithiocarbamate and piperidinium piperidine-1-carbodithioate, respectively. These compounds have been obtained as colorless crystals in good isolated yields.

The structure of dithiocarbamates **2** has been proved by analytical and spectral data (table 1). The $^{1}$H NMR spectra indicate a shift for the signal of α-CH to the carbonyl group up to 5.7ppm. Also, new signals are recorded in the aliphatic area corresponding to the *N,N*-dialkylamino moieties. $^{13}$C NMR spectra indicate the appearance of a new signal at 203ppm, attributed to the thiocarbonyl group. The mass spectra also confirm the replacement of the α-bromine atom by dithiocarbamate units providing the following molecular ions ($M^+$, a.m.u.): 346.96 ($C_{12}H_{14}{}^{79}BrNO_2S_2$) for **2a**, 374.99 ($C_{14}H_{18}{}^{79}BrNO_2S_2$) for **2b**, and 386.99 ($C_{15}H_{18}{}^{79}BrNO_2S_2$) for **2c**.




**3 a-c** **4 a-c**

Scheme 2. Synthesis of mesoionic phenolates **4** and their interconversion with the corresponding 1,3-dithiolium hydrogen sulphates **3**

A concentrated sulfuric acid - glacial acid acetic acid (1:3 v/v) mixture was used for the cyclization of dithiocarbamates **2a-c** under mild reaction conditions (scheme 1) [20, 23, 65]. After 10 min at 80°C the homogeneous reaction mixture was cooled to room temperature and water was added. Filtration and recrystallization of the precipitate gives hydrogen sulphates **3a-c** as colorless crystals, in good yields (table 2). The cyclization of dithiocarbamates **2** was accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1640cm$^{-1}$) and the presence of new, strong and broad absorption bands at 1000-1100cm$^{-1}$, corresponding to the hydrogen sulphate anion. The $^{1}$H NMR spectra of 1,3-dithiol-2-ylium hydrogen sulphates indicate the absence of the quartet signal of *a*-carbonyl hydrogens from compounds **2** (ca. 5.7ppm). $^{13}$C NMR spectra also support the synthesis of 1,3-dithiolium salts **3** by the disappearance of the signals of carbonyl and thiocarbonyl carbon atoms present in the dithiocarbamates spectra and the appearance of a new signal at a very low field (ca. 183ppm) which correspond to the electron deficient C(2) atom. The mass spectra indicated the heterocyclization of dithiocarbamates showing the following molecular ions ($M^+$-$HSO_4^-$, a.m.u.): 329.96 ($C_{12}H_{13}{}^{79}BrNOS_2$) for **3a**, 357.99 ($C_{14}H_{17}{}^{79}BrNOS_2$) for **3b**, and 369.99 ($C_{15}H_{17}{}^{79}BrNOS_2$) for **3c**.

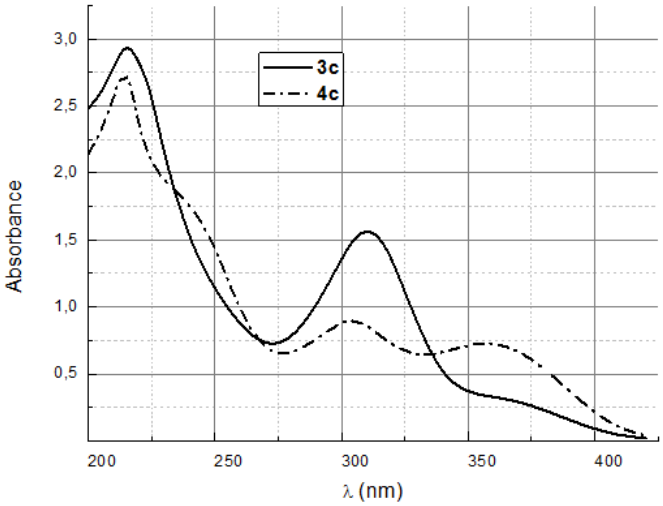



Fig. 1. UV-Vis absorption spectra of 4-(5-bromo-2-hydroxyphenyl)-5-methyl-2-(*N*-piperidinyl)-1,3-dithiol-2-ylium hydrogen sulphate (**3c**) and 4-bromo-2-[5-methyl-2-(*N*-piperidinyl)-1,3-dithiol-2-ylium-4-yl]phenolate **(4c)** in ethanol

Under heterogeneous conditions the treatment of hydrogen sulphates **3a-c** with saturated aqueous sodium hydrogen carbonate solution has provided 4-bromo-2-[5-methyl-2-(*N,N*-dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **4a-c**, 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 phenolates **4** with sulfuric acid regenerates the 1,3-dithiolium perchlorates **3** in quantitative yields (scheme 2).

It was previously reported that the presence of a hydroxy substituent in the *ortho*- or *para*-positions of the aromatic ring induce an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring [27,30]. Thus, 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. As mentioned above, phenolates **4** have been isolated as yellow products that present the features of mesoionic compounds [27]. The yellow color of mesoionic phenolates **4a-c** is also provided by an intramolecular charge transfer that was proved by measurement of UV-Vis absorption spectra at different concentrations.

The comparative analysis of the UV-Vis absorption spectra of 4-(5-bromo-2-hydroxyphenyl)-5-methyl-2-(*N*-piperidinyl)-1,3-dithiol-2-ylium hydrogen sulphate (**3c**) and 4-bromo-2-[5-methyl-2-(*N*-piperidinyl)-1,3-dithiol-2-ylium-4-yl]phenolate **(4c)** (fig. 1) indicate a hipsochromic shift of the n ® p* transition band from 310 nm in **3c** to 304 nm in **4c**. The spectrum of the mesoionic phenolate **4c** shows the charge transfer absorption band at 360 nm. As a result of the extended conjugation, the spectrum of mesoionic phenolate **4c** indicates a new absorption band at 240 nm that belongs to the contribution of the *ortho*-quinoid structure to the real state of the molecule.

## Conclusions

The synthesis of several of 4-(5-bromo-2-hydroxyphenyl)-5-methyl-2-(*N,N*-dialkylamino)-1,3-dithiol-2-ylium derivatives has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates

derived from propiophenone. The structure of new synthesized compounds has been proved by analytical and spectral (NMR, IR, UV-Vis, MS) data.

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