

Synthesis of Novel 4-Aryl-5-Methyl-1,3-Dithiolium Derivatives

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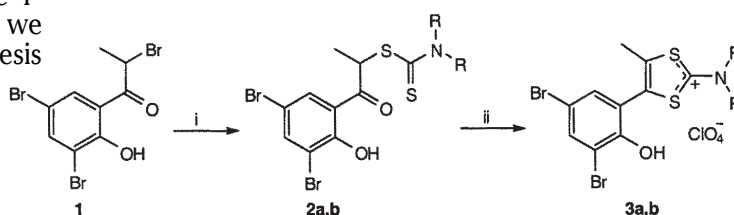
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Novel 4,6-dibromo-2-[5-methyl-2-(*N,N*-dialkylamino)-1,3-dithiol-2-yl]phenolates have been synthesized by the heterocondensation of the 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxopropan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the corresponding substituted α -bromopropiophenone with various salts of dithiocarbamic acids. The structure of 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxopropan-2-yl-piperidine-1-carbodithioate (**2b**) was unambiguously proved by X-ray crystallography.

Keywords: dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds, propiophenones, X-ray crystallography

Charge transfer complexes of tetrathiafulvalenes (TTF) with tetracyanoquinodimethane have attracted a special interest do to their good electrical conductivity [1, 2]. One of the most important class of precursors in the synthesis of tetrathiafulvalenes (TTF) is represented by 1,3-dithiolium salts [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 [17-22]. 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 [23, 24], we wish to extend these studies by presenting the synthesis of novel 4-aryl-5-methyl-1,3-dithiolium derivatives.

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



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

2, 3, 4	R	R
a	CH_3	CH_3
b	$(CH_2)_5$	

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 BioCary 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 ($\pm 0.27\%$) with the calculated values.

4-(3,5-Dibromo-2-hydroxyphenyl)-5-methyl-2-(piperidin-1-yl)-1,3-dithiol-2-yl]ium perchlorate (**3b**)

General Procedure

To a mixture of sulfuric acid (98%, 1.1mL) and glacial acetic acid (3.3mL), 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxopropan-2-yl-piperidine-1-carbodithioate (**2b**, 1.17g, 2.5mmol) was added in small portions. The reaction mixture was heated at 80 °C for 10min. After cooling, 70% $HClO_4$ (0.5mL) and then water (70mL) were added and the precipitate was filtered and dried off. Recrystallization

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	M.p., °C	η , %	IR-ATR, cm^{-1}	NMR (CDCl_3), ppm
2a	141 - 142	75	2924, 1638, 1431, 1305, 1247, 1131, 849, 781, 675, 568	$^1\text{H NMR } \delta$: 1.52 (3H, d, CH_3); 3.64 (3H, s, $\text{CH}_3\text{-N}$); 3.68 (3H, s, $\text{CH}_3\text{-N}$); 5.77 (1H, q, CH); 7.85 (1H, d, H-4); 8.19 (1H, d, H-6; $J_{\text{H4-H6}}=2.4$ Hz); 12.66 (1H, s, OH). $^{13}\text{C NMR } \delta$: 16.8, 44.4, 46.0, 50.5, 110.3, 113.8, 120.0, 132.5, 141.6, 158.9, 192.7, 202.5.
2b	134 - 135	83	2947, 1641, 1425, 1321, 1245, 1216, 1134, 842, 774, 667, 552	$^1\text{H NMR } \delta$: 1.61 (3H, d, CH_3); 1.69 (6H, m, 3CH_2); 3.85 (2H, m, $\text{CH}_2\text{-N}$); 4.23 (2H, m, $\text{CH}_2\text{-N}$); 5.77 (1H, q, CH); 7.84 (1H, d, H-4); 8.13 (1H, d, H-6; $J_{\text{H4-H6}}=2.3$ Hz); 12.65 (1H, s, OH). $^{13}\text{C NMR } \delta$: 16.6, 23.5, 25.0, 25.5, 43.1, 50.8, 52.4, 111.2, 113.4, 119.6, 131.7, 141.6, 158.5, 192.0, 202.8.

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

	M.p., °C	η , %	IR-ATR, cm^{-1}	NMR ($\text{DMSO-}d_6$), ppm
3a	185-186	67	3048, 2968, 1558, 1431, 1100, 1010, 858, 762, 564	$^1\text{H NMR } \delta$: 2.26 (3H, s, $\text{CH}_3\text{-5}$); 3.52 (3H, s, $\text{CH}_3\text{-N}$); 3.55 (3H, s, $\text{CH}_3\text{-N}$); 7.45 (1H, d, H-4); 7.79 (1H, d, H-6; $J_{\text{H4-H6}}=1.8$ Hz); 10.00 (1H, s, OH). $^{13}\text{C NMR } \delta$: 17.5, 47.3, 47.8, 112.0, 113.5, 117.0, 125.6, 132.5, 134.1, 137.5, 150.7, 185.1.
3b	172-173	74	3051, 1556, 1432, 1250, 1099, 995, 875, 614, 552	$^1\text{H NMR } \delta$: 1.80 (6H, m, 3CH_2); 2.28 (3H, s, $\text{CH}_3\text{-5}$); 3.86 (4H, m, 2CH_2); 7.45 (1H, d, H-4); 7.80 (1H, d, H-6; $J_{\text{H4-H6}}=1.8$ Hz); 10.15 (1H, s, OH). $^{13}\text{C NMR } \delta$: 17.3, 21.6, 24.8, 24.9, 56.5, 57.5, 112.1, 113.2, 117.9, 125.5, 133.1, 134.5, 137.4, 151.6, 185.4.

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

	M.p., °C	η , %	IR-ATR, cm^{-1}	NMR ($\text{DMSO-}d_6$), ppm
4a	205-206 dec.	100	2978, 1500, 1450, 1256, 1222, 850, 768, 710, 658	$^1\text{H NMR } \delta$: 2.25 (3H, s, $\text{CH}_3\text{-5}$); 3.50 (3H, s, $\text{CH}_3\text{-N}$); 3.53 (3H, s, $\text{CH}_3\text{-N}$); 7.40 (1H, d, H-4); 7.75 (1H, d, H-6; $J_{\text{H4-H6}}=1.9$ Hz). $^{13}\text{C NMR } \delta$: 17.4, 47.4, 47.8, 112.1, 113.6, 117.2, 125.5, 132.7, 134.0, 137.6, 150.4, 185.0.
4b	139-140 dec.	100	2974, 1520, 1440, 1233, 1138, 840, 710, 656	$^1\text{H NMR } \delta$: 1.80 (6H, m, 3CH_2); 2.26 (3H, s, $\text{CH}_3\text{-5}$); 3.84 (4H, m, 2CH_2); 7.43 (1H, d, H-4); 7.77 (1H, d, H-6; $J_{\text{H4-H6}}=1.9$ Hz). $^{13}\text{C NMR } \delta$: 17.6, 21.7, 24.8, 25.2, 56.4, 57.5, 112.0, 113.5, 118.2, 125.6, 133.0, 134.8, 137.6, 151.8, 185.5.

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

from EtOH (100mL) gave colorless crystals; yield 1.05g (74%). Analytical and spectral data of 1,3-dithiolium perchlorates **3a,b** are presented in table 2.

4,6-Dibromo-2-[5-methyl-2-(piperidin-1-yl)-1,3-dithiol-2-ylphenolate (**4b**);

General Procedure

To a saturated sodium hydrogen carbonate solution (10mL), perchlorate **3b** (0.5g, 0.8mmol) 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 ethanol gave yellow crystals; yield 0.46g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **4a,b** are presented in table 3.

c. X-ray Structure Determination of **2b**:

Numerical details are presented in table 4.

Single crystals of $\text{C}_{15}\text{H}_{17}\text{Br}_2\text{NO}_2\text{S}_2$ were obtained by recrystallization from ethanol. A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 294 K during data collection. Using Olex2 [25], the structure was solved with the ShelXS [26, 27] structure solution program using Direct Methods and refined with the ShelXL [28] refinement package using Least Squares minimization. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC xxxxxxx). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussions

Phenacyl carbodithioates are important precursors for the synthesis of 1,3-dithiolium salts and of their derivatives. The reactions of α -bromophenones with salts of dithiocarbamic acid, readily available from the reaction of secondary amine with carbon disulfide [29], represent the synthetic way to various substituted phenacyl carbodithioates. Following this reaction pathway, we obtained phenacyl dithiocarbamates **2a,b** by reacting 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)propan-1-one (**1**) [30] with sodium *N,N*-dimethyldithiocarbamate 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 $^1\text{H NMR}$ spectra indicate a shift in value for the quartet belonging to the α -carbonyl proton from around 2.5 ppm to 5.77 ppm. Also, new signals appear at high fields corresponding to the signals belonging to the rest of the protons in the dimethylamino and piperidine moieties. $^{13}\text{C NMR}$ spectra indicate the appearance of a new signal at 202 ppm, attributed to the thiocarbonyl group. The structure of 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxapropan-2-yl-piperidine-1-carbodithioate (**2b**) has unambiguously proved by X-ray crystallography (fig. 1). Crystal data are presented in table 4. The recorded data confirms the extended p - π conjugation at the level of dithiocarbamic group [31,32]; the length of N-C(10) bond is 1.320(4)Å, shorter than N-C(18) and N-C(22) that are essentially σ -bonds (1.47(4)Å). Intermolecular sulfur-bromine and oxygen-bromine interactions are present.

Using a concentrated sulfuric acid-glacial acetic acid (1:3v/v) mixture [33-35] the cyclocondensation of carbodithioates **2a,b** takes place. After 10min at 80 °C the homogeneous reaction mixture was cooled to room temperature and 70% HClO_4 and water were added. Filtration and recrystallization of the precipitate gives perchlorates **3** as colorless crystals, in good yields (table

$C_{15}H_{17}Br_2NO_2S_2$	$F(000) = 928$
$M_r = 467.23$	$D_x = 1.769 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 8.8600 (4) \text{ \AA}$	Cell parameters from 4772 reflections
$b = 14.3459 (5) \text{ \AA}$	$\theta = 3.6\text{--}24.7^\circ$
$c = 13.8600 (5) \text{ \AA}$	$\mu = 4.86 \text{ mm}^{-1}$
$\beta = 95.308 (3)^\circ$	$T = 294 \text{ K}$
$V = 1754.12 (11) \text{ \AA}^3$	Irregular, clear light colourless
$Z = 4$	$0.35 \times 0.22 \times 0.20 \text{ mm}$
SuperNova, Dual, Cu at zero, Eos diffractometer	4213 independent reflections
Radiation source: SuperNova (Mo) X-ray Source	3075 reflections with $I > 2\sigma(I)$
mirror	$R_{\text{int}} = 0.046$
Detector resolution: $8.0851 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 29.1^\circ$, $\theta_{\text{min}} = 3.2^\circ$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan <i>CrysAlis PRO</i> , Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171.NET) (compiled May 22 2014, 16:03:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -19 \rightarrow 19$
$T_{\text{min}} = 0.566$, $T_{\text{max}} = 1.000$	$l = -18 \rightarrow 18$
19619 measured reflections	
Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 1.6802P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4213 reflections	$\Delta_{\text{max}} = 0.70 \text{ e \AA}^{-3}$
201 parameters	$\Delta_{\text{min}} = -0.62 \text{ e \AA}^{-3}$
0 restraints	

Table 4
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR **2b**

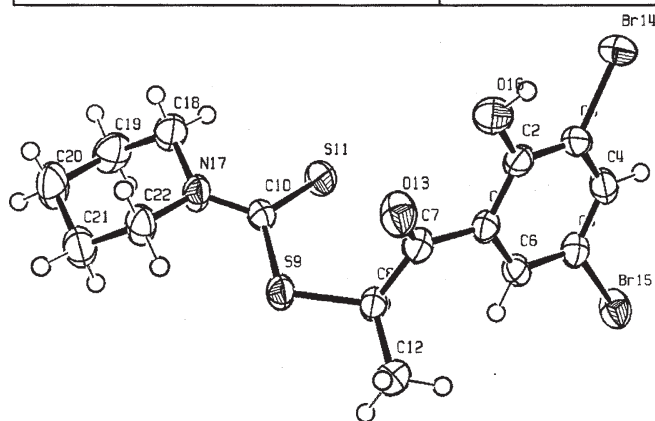
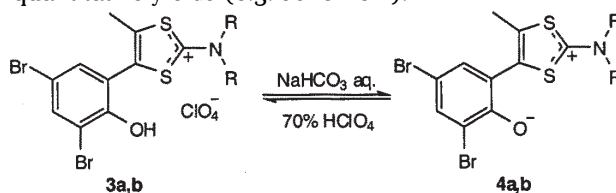


Fig. 1. Molecular structure of dithiocarbamate **2b**. Ellipsoids represent 50% probability levels. Selected molecular dimensions (\AA): N-C(10) 1.320(4), S(11)-C(10) 1.673(3), S(9)-C(10) 1.773(3), N-C(10)-S(11) 124.8(2), N-C(10)-S(9) 113.7(2), S(9)-C(10)-S(11) 121.48(19)

2). The cyclization of carbodithioates **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 $1100\text{--}1200\text{cm}^{-1}$, corresponding to the perchlorate anion. Heterocyclization of carbodithioates **2** is also supported by the NMR spectra. Thus, the ^1H NMR spectra of 1,3-dithiol-2-ylum perchlorate

indicate the absence of the α -carbonyl hydrogens from compounds **2** (5.7 ppm). ^{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. 185 ppm) which correspond to the electron deficient C-2 atom.

Treatment of perchlorates **3a,b**, under heterogeneous conditions, with saturated aqueous sodium hydrogen carbonate solution provides 3,5-dibromo-2-[5-methyl-2-(dialkylamino)-1,3-dithiol-2-ylum-4-yl]phenolates **4a,b**, 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 **4** with 70% HClO_4 regenerates the 1,3-dithiolium perchlorates **3** in quantitative yields (e.g. scheme 2).



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

The presence of a hydroxy substituent in the *ortho*- or *para*-positions induces an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring. In a previous paper [36], the comparative study of UV-Vis absorption spectra of 2-, 3-, and 4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-yl-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 before, phenolates **4** have been isolated as yellow products that present the features of mesoionic compounds [37]. The yellow color of mesoionic phenolates **4a,b** is also provided by an intramolecular charge transfer, that was proved by measurement of UV-Vis absorption spectra at different concentrations.

Conclusions

The synthesis of a series of 4-aryl-5-methyl-2-(*N,N*-dialkylamino)-1,3-dithiol-2-yl-ium derivatives has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates. The structure of new synthesized compounds has been proved by analytical and spectral (NMR, IR) data. X-Ray crystallography proved the structure of 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxapropan-2-yl-piperidine-1-carbodithioate. Crystallographic data revealed intermolecular bromine-sulfur and bromine-oxygen and an extended p - π conjugation at the level of dithiocarbamic group.

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