Synthesis of New 1,3-Dithiolium Derivatives from Propiophenones

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*Novel 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-2-(N,N-dialkylamino)-1,3-dithiol-2-ylium salts have been synthesized by the heterocondensation of the 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxapropan-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-oxapropan-2-yl-morpholine-4-carbodithioate (**2b**) was unambigously proved by X-ray crystallography. A strong intramolecular phenol O-H•••O hydrogen bond has been identified in this molecule.*

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

1,3-Dithiolium salts are well-known precursors of tetrathiafulvalenes (TTF) [1-4]. The famous charge transfer salts of tetrathiafulvalenes (TTF) with tetracyanoquinodimethane have attracted general interest due to their quasi-metallic electrical conductivity [5, 6]. Recent reports highlighted the TTFs ability to act as donor groups in intramolecular charge-transfer complexes [7, 8]. A variety of acceptor units have been investigated, nitrogen and sulfur containing cations receiving a great deal of attention [9-17]. Of special interest are systems where the donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety [18-22]. 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 [24, 25]. Along with the applications in material chemistry [26], 1,3-dithiolium cations exhibit interesting properties for medicinal chemistry. 1,3-Dithiolium systems are known for their reactivity at the C(2)-position towards nucleophiles [27]. Moreover, this type of compounds has been found to exhibit biological activity, in a particular case, against gram-positive and gram-negative bacteria [28-31].

Following our previous investigation on the synthesis of some 4-(hydroxyaryl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts from the corresponding α-haloketones [9-11], we wish to extend these studies by presenting a new class of 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-2-(*N,N*-dialkylamino)-1,3-dithiolium salts and the corresponding mesoionic 4,6-dibromo-2-(5-methyl-1,3-dithiolim-2-yl)phenolates.

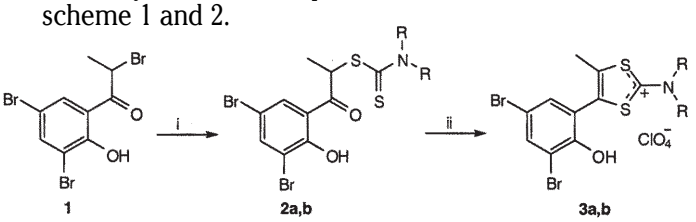
Experimental part

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 (±0.35%) with the calculated values.

b. Synthesis

The synthesis of compounds **2**, **3** and **4** is described in scheme 1 and 2.



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	$-CH_2CH_3$	$-CH_2CH_3$
b	$-(CH_2)_2-O-(CH_2)_2-$	

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

1-(3,5-Dibromo-2-hydroxyphenyl)-1-oxapropan-2-yl-morpholine-4-carbodithioate (**2b**)

General Procedure

To a solution of 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)propan-1-one (**1**, 3.87g, 0.01mol) in acetone (100mL), a solution of morpholinium morpholine-4-carbodithioate (2.5g, 0.01mol) in acetone-water (1:1, 70mL) was added. The reaction mixture was refluxed for 10min, cooled to room temperature and then poured in water. The precipitate was filtered, washed with water and dried off. Recrystallization from EtOH (100mL) gave colorless crystals; yield 3.75g (80%). Analytical and spectral data of carbodithioates **2a, b** are presented in table 1.

4-(3,5-Dibromo-2-hydroxyphenyl)-5-methyl-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate (**3b**)

General Procedure

To a mixture of sulfuric acid (98%, 2.35mL) and glacial acetic acid (7mL), 1-(3,5-dibromo-2-hydroxyphenyl)-1-

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	M.p. (°C)	η (%)	IR-ATR (cm^{-1})	NMR ($CDCl_3$) (ppm)
2a	136 - 137	79	2947, 1642, 1435, 1318, 1252, 1211, 1138, 851, 783, 698, 550	*^1H NMR* δ : 1.28 (3H, t, CH_3); 1.29 (3H, t, CH_3); 1.61 (3H, d, CH_3); 3.72 (2H, q, CH_2-N); 4.00 (2H, q, CH_2-N); 5.76 (1H, q, CH); 7.85 (1H, d, H-4); 8.14 (1H, d, H-6; J_{H4-H6}=2.3 Hz); 12.65 (1H, s, OH). *^{13}C NMR* δ : 11.4, 12.5, 16.7, 47.4, 49.5, 50.7, 110.5, 113.7, 119.9, 132.0, 141.4, 158.7, 192.5, 202.4 .
2b	116 - 117	80	2952, 1647, 1439, 1322, 1248, 1218, 1135, 850, 785, 680, 544	*^1H NMR* δ : 1.62 (3H, d, CH_3); 3.77 (4H, m, CH_2-O-CH_2); 3.93 (2H, m, CH_2-N); 4.28 (2H, m, CH_2-N); 5.77 (1H, q, CH); 7.57 (1H, d, H-4); 8.11 (1H, d, H-6; J_{H4-H6}=2.4 Hz); 12.59 (1H, s, OH). *^{13}C NMR* δ : 16.6, 50.9, 52.0, 53.8, 65.2, 110.7, 113.2, 119.7, 131.8, 141.5, 158.4, 192.1, 202.9 .

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

	M.p. (°C)	η (%)	IR-ATR (cm^{-1})	NMR (DMSO-d_6) (ppm)
3a	161-162	75	3052, 2980, 1561, 1439, 1102, 1011, 862, 778, 571	*^1H NMR* δ : 1.39 (3H, t, CH_3); 1.42 (3H, t, CH_3); 2.29 (3H, s, CH_3-5); 3.80 (2H, q, CH_2); 3.84 (2H, q, CH_2); 7.46 (1H, d, H-4); 7,80 (1H, d, H-6; J_{H4-H6}=1.7 Hz); 10.07 (1H, s, OH). *^{13}C NMR* δ : 17.4, 26.1, 26.4, 56.2, 56.9, 112.2, 113.4, 117.1, 125.5, 132.4, 134.1, 137.4, 150.9, 185.5 .
3b	228-229 dec.	77	3058, 1555, 1430, 1254, 1077, 880, 615, 548	*^1H NMR* δ : 2.26 (3H, s, CH_3-5); 3.88 (8H, m, 4CH_2); 7.45 (1H, d, H-4); 7.79 (1H, d, H-6; J_{H4-H6}=1.6 Hz); 10.03 (1H, s, OH). *^{13}C NMR* δ : 17.3, 54.3, 54.8, 64.5, 112.5, 113.3, 117.5, 125.8, 132.9, 134.3, 137.5, 151.1, 185.3 .

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

oxapropan-2-yl-morpholine-4-carbodithioate (**2b**, 2.35g, 5mmol) was added in small portions. The reaction mixture was heated at 80°C for 10min. After cooling, 70% $HClO_4$ (1mL) and then water (100mL) were added and the precipitate was filtered and dried off. Recrystallization from EtOH (200mL) gave colorless crystals; yield 2.12g (77%). Analytical and spectral data of 1,3-dithiolium perchlorates **3a, b** are presented in table 2.

4,6-Dibromo-2-[5-methyl-2-(morpholin-4-yl)-1,3-dithiol 2-ylium-4-yl]phenolate (**4b**);
General procedure

To a saturated sodium hydrogen carbonate solution (20mL), perchlorate **3b** (1g, 1.8mmol) 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 ethanol gave yellow crystals; yield 0.81g (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.

The intensity data of **2b** was collected on a Stoe IPDS 2T diffractometer with MoK_α radiation. The data were collected with the Stoe XAREA program using ω-scans [32]. The space groups were determined with the XRED32 program [32]. The structures were solved by direct

	M.p. (°C)	η (%)	IR-ATR (cm^{-1})	NMR (DMSO-d_6) (ppm)
4a	197-198 dec.	100	2970, 1548, 1501, 1452, 1263, 1228, 1133, 855, 761, 712, 660, 558	*^1H NMR* δ : 1.39 (3H, t, CH_3); 1.42 (3H, t, CH_3); 2.27 (3H, s, CH_3-5); 3.78 (2H, q, CH_2); 3.82 (2H, q, CH_2); 7.44 (1H, d, H-4); 7.78 (1H, d, H-6; J_{H4-H6}=1.9 Hz). *^{13}C NMR* δ : 17.4, 26.0, 26.4, 56.1, 56.7, 112.0, 113.5, 117.0, 125.6, 132.5, 134.2, 137.7, 151.1, 185.3 .
4b	133-134 dec.	100	2944, 1550, 1498, 1445, 1248, 1135, 848, 711, 660	*^1H NMR* δ : 2.25 (3H, s, CH_3-5); 3.87 (8H, m, 4CH_2); 7.43 (1H, d, H-4); 7.77 (1H, d, H-6; J_{H4-H6}=1.9 Hz). *^{13}C NMR* δ : 17.2, 54.4, 54.7, 64.4, 112.4, 113.5, 117.3, 125.7, 132.7, 134.4, 137.6, 151.0, 185.4 .

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

Identification code	ip330	
Empirical formula	$C_{14}H_{15}Br_2NO_3S_2$	
Formula weight	469.21	
Temperature	153(2)K	
Wavelength	0.71073Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.670(2)Å	α= 90°
	b = 10.064(2)Å	β= 97.17(3)°
	c = 14.211(3)Å	γ = 90°
Volume	1656.1(6)$Å^3$	
Z	4	
Density (calculated)	1.882Mg/m^3	
Absorption coefficient	5.157mm^{-1}	
F(000)	928	
Crystal size	0.48x0.24x0.24mm^3	
Theta range for data collection	2.13 to 28.28°	
Index ranges	-13<=h<=15, -12<=k<=13, -18<=l<=18	
Reflections collected	11362	
Independent reflections	4082 [R(int) = 0.0719]	
Completeness to theta = 28.28°	99.2%	
Absorption correction	Sphere	
Max. and min. transmission	0.0682 and 0.0425	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4082 / 0 / 204	
Goodness-of-fit on F^2	1.111	
Final R indices [I > 2sigma(I)]	R1 = 0.0492, wR2 = 0.0838	
R indices (all data)	R1 = 0.0773, wR2 = 0.0909	
Largest diff. peak and hole	0.637 and -0.507e.$Å^{-3}$	

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

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.81(7)	1.76(7)	2.504(4)	152(7)

Table 5
HYDROGEN BONDS [Å and °]

methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97 [33, 34].

CCDC-1004208 contain the supplementary crystallographic data for compound **2b**. These 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 useful intermediates 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 [35], represent an accessible way to various substituted phenacyl carbodithioates. Following this synthetic strategy, we obtained phenacyl dithiocarbamates **2a, b** by reacting 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)propan-1-one (**1**) [36] with sodium *N*,*N*-diethyldithiocarbamate and morpholinium morpholine-4-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 in value for the quartet belonging to the α-carbonyl proton from around 2.5ppm to ca. 5.76ppm. Also, new signals appear at high fields corresponding to the signals belonging to the rest of the protons in the diethylamino and morpholine moieties. ^{13}C NMR spectra indicate the appearance of a new signal at 192ppm, attributed to the thiocarbonyl group. The structure of 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxa-propan-2-yl-morpholine-4-carbodithioate (**2b**) has unambigously proved by X-ray crystallography [37]. Crystal data are presented in table 4. A strong intramolecular phenol O(1)-H(1)•••O(2) hydrogen bond has been identified in this molecule (fig.1 and table 5). The recorded data confirms the extended *p*-π conjugation at the level of dithiocarbamic group [38, 39]; the lenght of N-C(9) bond is 1.338(4)A°, shorter than N-C(10) and N-C(13) that are essentially σ-bonds (1.46(5)A°). The dihedral angle between the plane of the phenol group and that of the planar section of the morpholine-4-carbodithiolate moiety is 71.4(3)°.

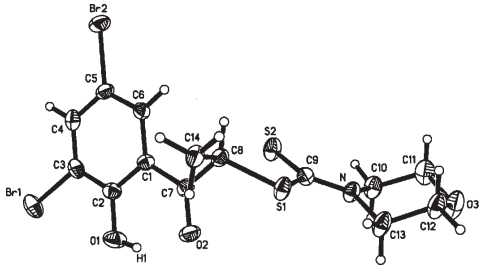
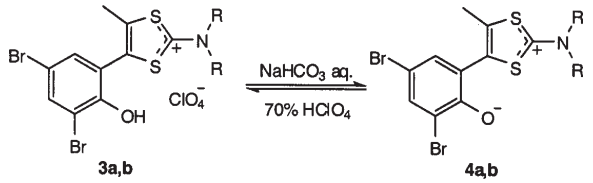


Fig. 1. Molecular structure of compound **2b**. Ellipsoids represent 50% probability levels. Selected molecular dimensions (A°, °): N-C(9) 1.338(4), S(1)-C(9) 1.771(4), S(2)-C(9) 1.656(4), N-C(9)-S(2) 125.0(3), N-C(9)-S(1) 113.4(3), S(2)-C(9)-S(1) 121.6(2) .

Using a concentrated sulfuric acid-glacial acetic acid (1:3 v/v) mixture [40-42] the cyclization of dithiocarbamates **2a, b** takes place under mild reaction conditions. 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 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 1100-1200cm^{-1}, corresponding to the perchlorate anion. Heterocyclization of dithiocarbamates **2** is also supported by the NMR spectra. Thus, the ^{1}H NMR spectra of 1,3-dithiol-2-ylium perchlorate indicate the absence of the α-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 carbonyl and thiocarbonyl carbon atoms present in the dithiocarbamates spectra and the appearance of a new signal at a very low field (185ppm) 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-ylium-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 (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 induce an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring. In a previous paper [24], 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 colour 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 [43]. The yellow colour 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-(3,5-dibromo-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. X-Ray crystallography proved the structure of 1-(3,5-dibromo-2-

hydroxyphenyl)-1-oxapropan-2-yl-morpholine-4-carbodithioate. Crystallographic data revealed a strong intramolecular phenol O-H•••O hydrogen bond and an extented *p*-π conjugation at the level of dithiocarbamic group.

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