New Bromo Substituted 1,3-Dithiol-2-ylium Salts

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*A series of 5-bromo-2-(N,N-dimethylamino)-1,3-dithiol-2-ylium compounds have been synthesized by the bromination of the corresponding 6-[2-(N,N-dimethylamino)-1,3-dithiol-2-ylium-4-yl]phenolates at the C(5) position of the 1,3-dithiol ring. The latter compounds have been obtained by heterocyclofunctionalization of some xylenols. The structure of 5-bromo-4-(3-bromo-4,5-dimethyl-2-hydroxyphenyl)-2-(N,N-dimethylamino)-1,3-dithiol-2-ylium bromide (**7a**) was unambigously proved by X-ray crystallography.*

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

One of the most important features of heterocyclic compounds is represented by their versatility to carry various substituents within a well defined three dimensional space [1, 2]. Along with a large variety of industrial application, heterocyclic compounds exhibit a strong implication in therapeutics [5-9]. Nitrogen or/and sulfur containing heterocyclic compounds have received a particular interest among researchers [10-17]. A special attention has been devoted to 1,3-dithiolium derivatives, compounds that are known for their reactivity at the C(2)-position towards nucleophiles [18]. Besides the synthetic interest for these reactions, 1,3-dithiolium salts are important precursors in the synthesis of tetrathiafulvalenes (TTF), the latter being good π-electron donors for organic metals [19]. Recent studies underlined the role of TTFs as donor groups in intramolecular charge-transfer complexes [20]. In this context, a variety of acceptor units has been investigated, special attention being devoted to the nature of cationic systems. Thus, of special interest are systems where the donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety [21-29]. Recently, new evidences for the mesoionic character of 2-(1,3-dithiol-2-ylium)phenolates (*Iasinones*) have reported reported [30]. These data have been obtained from bromination reactions of the 1,3-dithiolium ring. An electrophilic addition of bromine at the 5th position indicated an extended delocalization of the negative charge. In order to extend this study, we are reporting here the synthesis of several 5-bromo-2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium derivatives by the bromination of the corresponding 6-[2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]phenolates at the C(5) position of the 1,3-dithiol ring.

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 and S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.31%) with the calculated values.

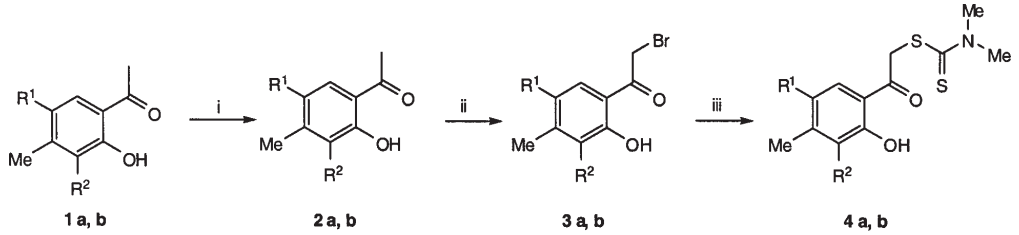
b. Synthesis

The reaction sequence for the synthesis of starting materials for the target compounds is described in scheme 1.

4-Bromo-6-[2-(N,N-dimethylamino)-1,3-dithiol-2-ylium-4-yl]-2,3-dimethylphenolate (**6b**)

General Procedure

To a saturated sodium hydrogen carbonate solution (20mL), perchlorate **5b** [31] (1g, 2.23mmol) 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 yellow



i. Br_2, aq. AcOH (66%), reflux; ii. Br_2, gl. AcOH, reflux; iii. $Me_2NC(S)S^-$, acetone, reflux

Scheme 1. Synthesis of precursors **1-4**

1, 2, 3, 4	R^1	R^2
a	Me	Br
b	Br	Me

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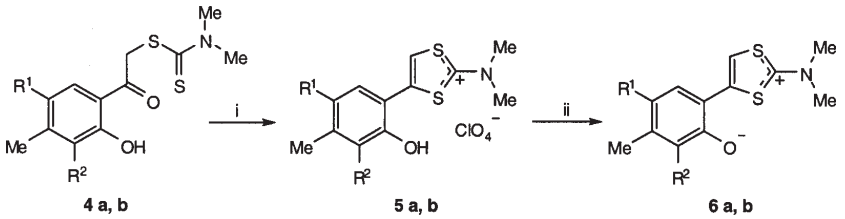


i. H_2SO_4/AcOH 1:3 (v/v), 80 °C, 70% $HClO_4$; ii. $NaHCO_3$ (aq)

Scheme 2. Synthesis 1,3-dithiolium perchlorates **5** and mesoionic phenolates **6**

5, 6, 7, 8	R^1	R^2
a	Me	Br
b	Br	Me

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
6b	243-244 dec.	100	3352, 2514, 1548, 1482, 1421, 1179, 925, 851	*^1H NMR* δ : 2.21 (3H, s, CH_3-3); 2.32 (3H, s, CH_3-4); 3.58 (3H, s, CH_3-N); 3.59 (3H, s, CH_3-N); 7.70 (1H, s, H-6); 8.05 (1H, s, H-5). *^{13}C NMR* δ : 15.5, 19.8, 44.5, 45.4, 118.3, 119.2, 127.9, 131.8, 131.9, 137.4, 139.6, 151.1, 185.9.

Table 1
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATE **6b**

crystals; yield 0.77g (100%). Analytical and spectral data are presented in table 1.

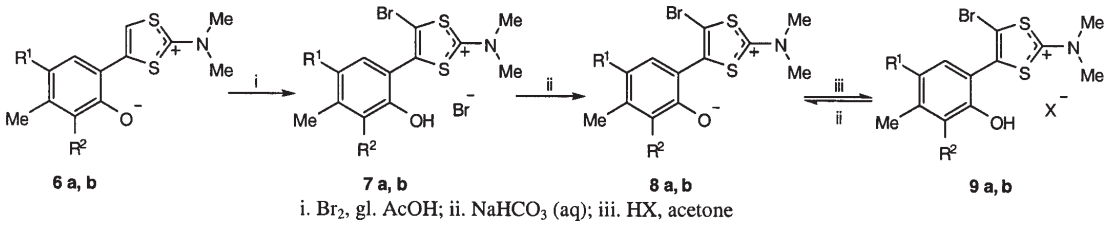
*5-Bromo-4-(5-bromo-3,4-dimethyl-2-hydroxyphenyl)-2-(N,N-dimethylamino)-1,3-dithiol-2- ylium bromide (**7b**) General Procedure*

To a solution of phenolate **6b** (0.5g, 1.45mmol) in glacial acetic acid (30mL) a solution of bromine (0.075mL, 1.45mmol) in glacial acetic acid (2mL) was added dropwise at room temperature. A precipitate was formed, that was filtered off, washed with water, and dried. Recrystallization from ethanol (20mL) gave colorless crystals; yield 0.6g (83%). Analytical and spectral data of 1,3-dithiolium bromides **7** are presented in table 2.

Mesoionic phenolates **8a** and **8b** have been synthesized in accordance with the general procedure described for phenolate **6b**. Analytical and spectral data of 1,3-dithiolium phenolates **8** are presented in table 3.

*5-Bromo-4-(3-bromo-4,5-dimethyl-2-hydroxyphenyl)-2-(N,N-dimethylamino)-1,3-dithiol-2-ylium perchlorate (**9a**) General Procedure*

To a suspension of mesoionic phenolate **8a** (1g, 2.35mmol) in acetone (10mL) a solution of 1.22mL $HClO_4$ (70%, 0.5mL) was added. The reaction mixture was vigorously stirred at room temperature for 2h, then filtered and washed with acetone. Recrystallization from ethanol gave colorless crystals; yield 1.23g (100%). 1,3-Dithiolium hydrogen sulphate **9b** was obtained following the same experimental procedure, using 98% sulfuric acid instead



i. Br_2, gl. AcOH; ii. $NaHCO_3$ (aq); iii. HX, acetone

Scheme 3. Synthesis 1,3-dithiolium salts **7** and **9** and mesoionic phenolates **8**

9	R^1	R^2	X
a	Me	Br	ClO_4
b	Me	Br	HSO_4

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
7a	223 - 224 dec.	88	3348, 2940, 1581, 1476, 1333, 848	*^1H NMR* δ : 2.36 (3H, s, CH_3-4); 2.43 (3H, s, CH_3-5); 3.63 (3H, s, CH_3-N); 3.68 (3H, s, CH_3-N); 7.28 (1H, d, H-6); 10.18 (1H, s, OH). *^{13}C NMR* δ : 15.8, 20.3, 44.3, 45.7, 111.1, 119.1, 128.1, 131.4, 132.3, 137.4, 138.6, 151.3, 185.1.
7b	215 - 216 dec.	83	3347, 2932, 1580, 1459, 1304, 870	*^1H NMR* δ : 2.22 (3H, s, CH_3-3); 2.35 (3H, s, CH_3-4); 3.61 (3H, s, CH_3-N); 3.65 (3H, s, CH_3-N); 7.67 (1H, s, H-6), 10.08 (1H, s, OH). *^{13}C NMR* δ : 15.8, 19.5, 44.3, 45.4, 111.4, 119.0, 128.0, 131.9, 131.8, 137.1, 139.9, 151.4, 185.5.

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM BROMIDES **7**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
8a	173-174 dec.	100	3378, 2525, 1550, 1474, 1429, 1179, 925, 854	*^1H NMR* δ : 2.35 (3H, s, CH_3-4); 2.43 (3H, s, CH_3-5); 3.63 (6H, s, $2CH_3$-N); 7.27 (1H, d, H-6). *^{13}C NMR* δ : 15.7, 20.3, 44.3, 45.6, 111.2, 119.0, 128.4, 131.4, 132.5, 137.4, 138.7, 151.6, 185.2.
8b	175-176 dec.	100	3348, 2548, 1563, 1445, 1422, 1181, 954, 851	*^1H NMR* δ : 2.24 (3H, s, CH_3-3); 2.36 (3H, s, CH_3-4); 3.63 (3H, s, CH_3-N); 3.64 (3H, s, CH_3-N); 7.64 (1H, s, H-6). *^{13}C NMR* δ : 15.7, 19.8, 44.4, 45.5, 111.3, 118.8, 127.9, 131.5, 131.6, 137.0, 140.1, 151.2, 185.6.

Table 3
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES **8**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
9a	225 - 226 dec.	100	3348, 2939, 1585, 1479, 1333, 1098 (br), 844	^1H *NMR* δ : 2.36 (3H, s, CH_3-4); 2.44 (3H, s, CH_3-5); 3.63 (3H, s, CH_3-N); 3.65 (3H, s, CH_3-N); 7.29 (1H, d, H-6); 10.07 (1H, s , OH). ^{13}C *NMR* δ : 15.5, 20.1, 44.4, 45.7, 111.3, 119.1, 128.3, 131.5, 132.4, 137.5, 138.7, 151.5, 185.2.
9b	219 - 220 dec.	99	3362, 2947, 1581, 1458, 1314, 1090 (br), 875	^1H *NMR* δ : 2.36 (3H, s, CH_3-4); 2.43 (3H, s, CH_3-5); 3.62 (3H, s, CH_3-N); 3.67 (3H, s, CH_3-N); 5.86 (2H, s, OH + HSO_4); 7.29 (1H, d, H-6). ^{13}C *NMR* δ : 15.6, 20.2, 44.3, 45.5, 111.2, 119.2, 128.3, 131.4, 132.6, 137.7, 138.8, 151.7, 185.2.

Table 4
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM SALTS

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ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM SALTS **9**

$C_{13}H_{14}Br_2NOS_2 \cdot Br$	$Z = 2$
$M_r = 504.10$	$F(000) = 488$
Triclinic, P^-1	$D_x = 1.956 Mg \cdot m^{-3}$
$a = 7.5818(5)$Å	Mo $K\alpha$ radiation, $\lambda = 0.7107$Å
$b = 7.7461$ (5) Å	Cell parameters from 3007 reflections
$c = 15.4279$ (10) Å	$\theta = 3.5–25.1°$
$\alpha = 75.804(5)°$	$\mu = 7.31 mm^{-1}$
$\beta = 85.223$ (5)°	$T = 294$ K
$\gamma = 77.057$ (5)°	Prism, clear light yellow
$V = 855.70$ (10) Å^3	0.35×0.08×0.06mm
SuperNova, Dual, Cu at zero, Eos diffractometer	4116 independent reflections
Radiation source: SuperNova (Mo) X-ray Source	2940 reflections with $I > 2\sigma(I)$
mirror	$R_{int} = 0.043$
Detector resolution: 8.0851pixels mm^{-1}	$\theta_{max} = 29.2°$, $\theta_{min} = 3.0°$
ω scans	$h = -9 \rightarrow 10$
Absorption correction: multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$k = -10 \rightarrow 10$
$T_{min} = 0.471$, $T_{max} = 1.000$	$l = -20 \rightarrow 21$
12012 measured reflections	
Refinement on F^2	Primary atom site location: iterative
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.098$	$w = 1/[\sigma^2(F_o^2)+(0.0346P)^2+0.3235P]$ where $P = (F_o^2+2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
4116 reflections	$\Delta)_{max} = 0.48$ e Å^{-3}
186 parameters	$\Delta)_{min} = -0.47$ e Å^{-3}
0 restraints	

Table 5
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **7a**

of perchloric acid. Analytical and spectral data of 1,3-dithiolium salts **9a** and **9b** are presented in table 4.

*c. X-ray Structure Determination of **7a**:*

Single crystals of $C_{13}H_{14}Br_3NOS_2$ (C13 H14 Br2 N1 O1 S2 1+, Br1 1-) were obtained by re-crystallization from ethanol. A suitable single crystal was selected and measured on a SuperNova, Dual, Cu at zero, Eos diffractometer. The data were collected using Olex2 [32]; the structure was solved with the Superflip [33] structure solution program using Charge Flipping and refined with the ShelXL [34] refinement package using Least Squares minimisation. Numerical details are presented in table 5.

CCDC-1008555 contain the supplementary crystallographic data for compound **7a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cede.cam.ac.uk / data_request / cif.

Results and discussions

The main precursors for the synthesis of target compounds are 2-bromo-6-[2-(*N,N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]-3,4-dimethylphenolate (**6a**) and 4-bromo-6-[2-(*N,N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]-2,3-dimethylphenolate (**6b**). Their synthetic strategy involves three steps: the synthesis of the corresponding phenacyl carbodithioates, followed by their cyclo-condensation under acidic conditions and finally, conversion of the 1,3-dithiolium salts to the corresponding mesoionic phenolates **6a** and **6b**. The synthetic pathway required to accomplish the first step is described in scheme 1. 2-Bromo-1-(3-bromo-4,5-dimethyl-2-hydroxyphenyl) ethan-1-one (**3a**) has been synthesized using 1-(4,5-dimethyl-2-hydroxyphenyl)ethan-1-one (**1a**) as starting material [35]. The stepwise regioselective bromination of the aromatic core in cloroform and of the side chain in glacial acetic acid provided 1-(3-bromo-4,5-dimethyl-2-

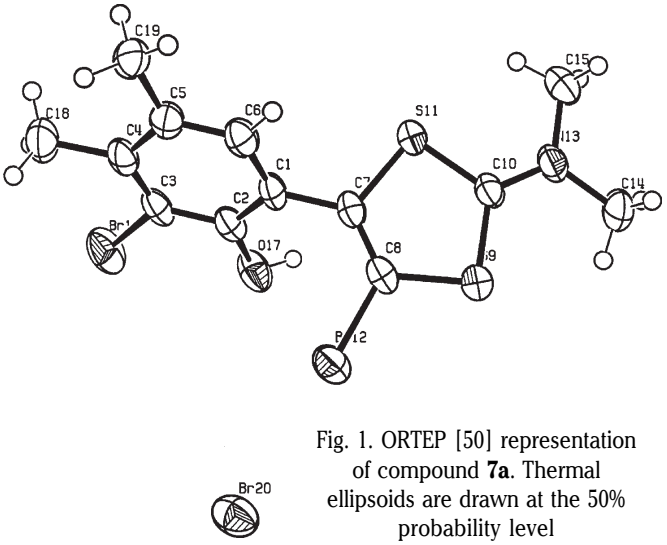

Fig. 1. ORTEP [50] representation of compound **7a**. Thermal ellipsoids are drawn at the 50% probability level

hydroxyphenyl)ethan-1-one (**2a**) and the target compound **3a**, respectively [31]. 2-Bromo-1-(5-bromo-3,4-dimethyl-2-hydroxyphenyl)ethan-1-one (**3b**) has been obtained from 1-(3,4-dimethyl-2-hydroxyphenyl)ethan-1-one (**1b**) [36, 37] following the double regioselective bromination procedure described above [31]. The salts of dialkyldithiocarbamic acid are readily available from the reaction of secondary amine with carbon disulfide [38]. The reactions of these compounds with α-bromophenones represent a useful method for the synthesis of a large variety of phenacyl carbodithioates [39-42]. Thus, phenacyl dithiocarbamates **4a**, **b** have been obtained by reacting ω-bromo-acetophenones **3a** and **3b** with dimethylamonium *N*,*N*-dimethyldithiocarbamate.

As mentioned before, the second step, the synthesis of 1,3-dithiol-2-ylium salts, consists in acid catalyzed cyclocondensation of phenacyl carbodithioates. A literature survey indicated several synthetic methods, including those for sensitive starting materials, used to accomplish the cyclization of various carbodithioates [43-47]. Using a mixture of concentrated sulfuric acid-glacial acetic acid (1:3 v/v) the cyclization of dithiocarbamates **4a** and **4b** takes place under mild reaction conditions. After 10min 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 provides 1,3-dithiolium perchlorates **5a** and **5b** as colorless crystals, in good to excellent yields (scheme 2) [31]. Treatment of perchlorates **5a** and **5b**, under heterogeneous conditions, with saturated aqueous sodium hydrogencarbonate solution gives 2-[2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **6a** and **6b**, in quantitative yields (Scheme 2). Analytical and spectral data of 4-bromo-6-[2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]-2,3-dimethylphenolate (**6b**) are presented in table 1.

Bromination of phenolates **6a** and **6b** takes place at the C5 position of the 1,3-dithiol ring (scheme 3). The structure of 1,3-dithiolium bromides **7a** and **7b** has been proved by analytical and spectral data (table 2). The NMR spectra support the bromination of phenolates **6** by the absence of the signal for the hydrogen atoms from the C(5) of the 1,3-dithiolium ring. Furthermore, the structure of 5-bromo-4-(3-bromo-4,5-dimethyl-2-hydroxyphenyl)-2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium bromide (**7a**) was unambiguously proved by X-ray crystallography (fig. 1) [48]. In this salt, the benzene and 1,3-dithiolium planes form a dihedral angle of 120.58°, a significantly higher deviation than that previously reported for a similar compound [49]. Most likely, this deviation from planarity appears due to the bulky bromine substituent in the 5-position of 1,3-dithiolium ring. Moreover, no hydrogen bond was found between the phenolic O—H group and the sulfur atoms. Instead, a hydrogen bond between the O—H group and the bromide counter-anion is present. Also present in the crystal is a short intermolecular Br(12)···Br(20) interaction (3.212 A°). The recorded data confirms the double bonding character of the C(10)-N(13) bond (numbering from fig. 1); the lenght of N(13)-C(10) bond is 1.309 A°, shorter than N(13)-C(14) and N(13)-C(15) that are essentially σ-bonds (1.469 A°).

Treatment of bromides **7a** and **7b**, under heterogeneous conditions, with saturated aqueous sodium hydrogencarbonate solution provides 2-[5-bromo-2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **8a** and **8b**, in quantitative yields (scheme 3). The structure of the new compounds has been proved by analytical and spectral data (table 3) and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compound **8a** with 70% perchloric acid generates the 1,3-dithiolium perchlorates **9a** in quantitative yields (scheme 3). In a similar manner by treating mesoionic phenolate **8a** with sulfuric acid, 1,3-dithiolium hydrogen sulphate **9b** has been isolated. The structure of the new salts **9a** and **9b** has been proved by analytical and spectral data (table 4).

Conclusions

The synthesis of several of 5-bromo-2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium compounds has been accomplished by the bromination of the corresponding 6-[2-(*N*,*N*-dimethylamino)-1,3-dithiol-2-ylium-4-yl]phenolates at the C(5) position of the 1,3-dithiol ring. The latter compounds have been obtained by heterocyclofunctionalization of some xylenols. The structure of 1,3-dithiol-2-ylium bromide **7a** was unambigously proved by X-ray crystallography.

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