Synthesis of 4-(4-Hydroxyaryl)-1,3-Dithiolium Perchlorates

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4-(3,5-Dibromo-4-hydroxyphenyl)-2-(N,N-dialkylamino)-1,3-dithiol-2-ylium perchlorates have been synthesized by acid catalyzed cyclocondensation of 1-(3,5-dibromo-4-hydroxyphenyl)-1-oxaethan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the corresponding substituted w-bromoacetophenone with various salts of dithiocarbamic acids.

Keywords: acetophenones, charge-transfer, dithiocarbamates, 1,3-dithiolium salts mesoionic compounds

Heterocycles represent a unique class of compounds that exhibit a large range of applications [1-3]. Amongst these, sulphur and nitrogen-containing heterocycles receive a great deal of attention, especially in the field of material chemistry [4-16]. These types of compounds also exhibit biological applications [17-26]. Organic *p*-donors and their cation radical salts have been studied extensively because of their potential as molecular conductors and superconductors [27-30]. The high electrical conductivity reported for the tetrathiafulvalene (TTF) complex with tetracyanoquinodimethane prompted the discovery of a variety of electron *p*-donors of the tetrathiafulvalene series [31 - 33]. In general, charge-transfer [34 - 42] or push-pull [43 - 53] compounds have important applications in the field of conducting materials. Of special interest are systems where the donor moiety is linked through a *p*- or *s*-bonded bridge to the acceptor moiety. 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 [54-56]. Following the previous investigation on the synthesis of 4-(hydroxyaryl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts from the corresponding *a*-haloketones [57, 58], we wish to extend these studies by presenting a new 4-(3,5-dibromo-4-hydroxyphenyl)-2-(*N,N*-dialkyl-amino)-1,3-dithiolium perchlorates and the corresponding mesoionic 2,6-dibromo-4-(1,3-dithiolim-2-yl)phenolates.

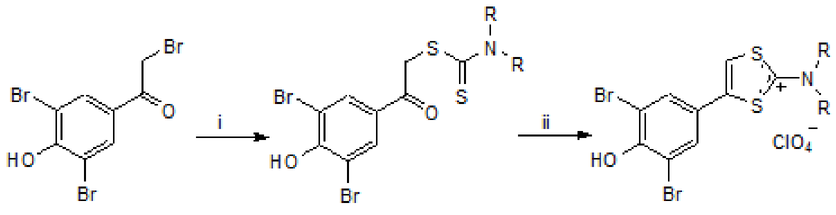
Experimental part

Analysis methods

Melting points were obtained on a KSPI melting-point meter and are uncorrected. IR spectra were recorded on a Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker 300 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, S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.3%) with the calculated values.

Synthesis

The synthetic pathway for the synthesis of carbodithioates **2a-e** and 1,3-dithiolium hydrogen perchlorates **3a-e** is described in scheme 1:



1 **2a-e** **3a-e**

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

2, 3, 4	R	R
a	CH_3	
b	CH_2CH_3	
c	$(CH_2)_4$	
d	$(CH_2)_5$	
e	$(CH_2)_2$-O-$(CH_2)_2$	

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

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Table 1

ANALYTICAL AND SPECTRAL DATA OF DITHIOCARBAMATES **2**

	M.p., °C	η, %	Spectral data
2a	207-208	72	^{1}H NMR ($CDCl_3$): δ = 3.88 (3H, s, CH_3); 3.92 (3H, s, CH_2-N); 4.75 (2H, s, CH_2); 8.15 (2H, d, Har-2 + Har-6; ^4J=2.1 Hz); 11.18 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 41.9, 44.3, 45.8, 112.1, 130.8, 133.0, 155.6, 190.1, 193.3 ppm. FT-IR (ATR): ν = 3298, 2950, 1644, 1489, 1420, 1308, 1248, 1211, 1122, 744, 658 cm^{-1}. MS (EI): *m/z* = 411 (M^+ for $C_{11}H_{11}{}^{79}Br_2NO_2S_2$).
2b	141-142	71	^{1}H NMR ($CDCl_3$): δ = 1.22 (3H, t, CH_3); 1.31 (3H, t, CH_3); 3.86 (2H, q, CH_2-N); 3.95 (2H, q, CH_2-N); 4.73 (2H, s, CH_2); 8.12 (2H, d, Har-2 + Har-6; ^4J=2.0 Hz); 11.15 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.5, 12.7, 43.5, 47.1, 49.5, 112.4, 130.6, 133.1, 155.7, 190.2, 193.1 ppm. FT-IR (ATR): ν = 3302, 2954, 1648, 1494, 1423, 1311, 1252, 1214, 1126, 743, 656 cm^{-1}. MS (EI): *m/z* = 439 (M^+ for $C_{13}H_{15}{}^{79}Br_2NO_2S_2$).
2e	206-207	82	^{1}H NMR ($CDCl_3$): δ = 3.67 (4H, m, CH_2-O-CH_2); 4.01 (2H, m, CH_2-N); 4.14 (2H, m, CH_2-N); 4.88 (2H, s, CH_2); 8.17 (2H, d, Har-2 + Har-6; ^4J=2.0 Hz); 10.14 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 43.8, 51.3, 52.0, 66.0, 112.1, 130.7, 133.0, 155.7, 190.2, 190.4 ppm. FT-IR (ATR): ν = 3310, 2957, 1647, 140, 1414, 1315, 1247, 1210, 1122, 740, 651 cm^{-1}. MS (EI): *m/z* = 453 (M^+ for $C_{13}H_{13}{}^{79}Br_2NO_2S_2$).

Table 2

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

	M.p., °C	η, %	Spectral data
3a	258-259 dec.	77	^{1}H NMR (DMSO-d_6): δ = 3.53 (3H, s, CH_3); 3.58 (3H, s, CH_3); 7.84 (2H, d, Har-2 + Har-6; ^4J=2.0 Hz); 7.97 (1H, s, H-5); 10.17 (1H, s, OH) ppm. ^{13}C NMR (DMSO-d_6): δ = 47.5, 47.8, 112.8, 119.3, 124.2, 130.8, 135.5, 153.1, 181.2 ppm. FT-IR (ATR): ν = 3047, 2962, 1541, 1441, 1101, 1008, 845, 768, 560 cm^{-1}. MS (EI): *m/z* = 394 (M^+-ClO_4 for $C_{11}H_{10}{}^{79}Br_2NOS_2$).
3b	217-218	75	^{1}H NMR (DMSO-d_6): δ = 1.35 (3H, t, CH_3); 1.38 (3H, t, CH_3); 3.85 (2H, q, CH_2); 3.90 (2H, q, CH_2); 7.85 (2H, d, Har-2 + Har-6; ^4J=2.1 Hz); 7.97 (1H, s, H-5); 10.13 (1H, s, OH) ppm. ^{13}C NMR (DMSO-d_6): δ = 17.7, 53.7, 54.4, 113.0, 119.3, 124.1, 130.9, 135.4, 153.2, 181.4 ppm. FT-IR (ATR): ν = 3040, 2958, 1538, 1438, 1111, 1004, 838, 764, 558 cm^{-1}. MS (EI): *m/z* = 422 (M^+-ClO_4 for $C_{13}H_{14}{}^{79}Br_2NOS_2$).
3c	252-253 dec.	72	^{1}H NMR (DMSO-d_6): δ = 2.25 (4H, m, 2CH_2); 3.72 (4H, m, 2CH_2); 7.86 (2H, d, Har-2 + Har-6; ^4J=2.0 Hz); 7.97 (1H, s, H-5); 10.11 (1H, s, OH) ppm. ^{13}C NMR (DMSO-d_6): δ = 26.0, 26.2, 56.5, 56.9, 113.0, 119.4, 124.3, 130.9, 135.8, 153.0, 180.9 ppm. FT-IR (ATR): ν = 3044, 2971, 1558, 1431, 1100, 1010, 858, 762, 564 cm^{-1}. MS (EI): *m/z* = 420 (M^+-ClO_4 for $C_{13}H_{12}{}^{79}Br_2NOS_2$).
3d	243-244 dec.	72	^{1}H NMR (DMSO-d_6): δ = 1.80 (6H, m, 3CH_2); 3.88 (4H, m, 2CH_2); 7.85 (2H, d, Har-2 + Har-6; ^4J=2.0 Hz); 7.99 (1H, s, H-5); 10.18 (1H, s, OH) ppm. ^{13}C NMR (DMSO-d_6): δ = 21.5, 24.8, 25.0, 56.5, 57.6, 112.9, 119.4, 124.0, 130.6, 135.7, 152.9, 181.2 ppm. FT-IR (ATR): ν = 3051, 1554, 1438, 1247, 1108, 998, 871, 611, 557 cm^{-1}. MS (EI): *m/z* = 434 (M^+-ClO_4 for $C_{14}H_{14}{}^{79}Br_2NOS_2$).
3e	252-253 dec.	73	^{1}H NMR (DMSO-d_6): δ = 3.88 (8H, m, 4CH_2); 7.87 (2H, d, Har-2 + Har-6; ^4J=2.0 Hz); 7.98 (1H, s, H-5); 10.20 (1H, s, OH) ppm. ^{13}C NMR (DMSO-d_6): δ = 54.0, 54.5, 64.4, 112.8, 119.3, 123.9, 130.5, 135.8, 153.1, 181.1 ppm. FT-IR (ATR): ν = 3044, 1551, 1431, 1245, 1112, 1014, 878, 620, 551 cm^{-1}. MS (EI): *m/z* = 436 (M^+-ClO_4 for $C_{13}H_{12}{}^{79}Br_2NO_2S_2$).

1-(3,5-Dibromo-4-hydroxyphenyl)-1-oxaethan-2-yl-morpholine-4-carbodithioate (**2e**); *General Procedure*

To a solution of 2-bromo-1-(3,5-dibromo-4-hydroxyphenyl)ethan-1-one (**1**, 1.5g, 4mmol) in acetone (20mL), a solution of morpholinium morpholine-4-carbodithioate (1g, 4mmol) in acetone-water (1:1, 30mL) 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 dioxane (10mL) gave colorless crystals; yield 1.49 g (82%). Analytical and spectral data of carbodithioates **2a**, **b**, **e** are presented in table 1.

4-(3,5-Dibromo-4-hydroxyphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate (**3e**); *General Procedure*

To a mixture of sulfuric acid (98%, 2mL) and glacial acetic acid (6mL), 1-(3,5-dibromo-4-hydroxyphenyl)-1-oxaethan-2-yl-morpholine-4-carbodithioate (**2a**, 1g, 2.2mmol) was added in small portions. The reaction mixture was heated at 80 °C for 10 min. After cooling, 70% $HClO_4$ (1mL) and water (100mL) were added and the precipitate was filtered and dried off. Recrystallization from DMF (5mL) gave colorless crystals; yield 0.86g (73%). Analytical and spectral data of 1,3-dithiolium perchlorates **3a-e** are presented in table 2.

2,6-Dibromo-4-[2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4e**)*;*

General Procedure

To a saturated sodium hydrogen carbonate solution (15mL), perchlorate **3e** (0.5g, 0.9 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 DMF gave yellow crystals; yield 0.4g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **4a**, **b**, **e** are presented in table 3.

Results and discussions

The synthetic strategy for the 4-(3,5-dibromo-2-hydroxyphenyl)-2-dialchilamino-1,3-dithiol-2-ylium perchlorates **3** is represented by the acid catalyzed cyclocondensation of the corresponding *N,N*-dialkyl-aminocarbodithioates [37, 38, 59]. The latter compounds are easily available from

Table 3

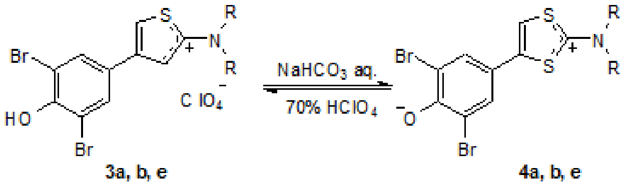
ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES **4**

	M.p., °C	η, %	Spectral data
4a	233-234 dec.	100	^{1}H NMR (DMSO-*d*$_6$): δ = 3.54 (6H, s, 2CH$_3$); 7.83 (2H, d, Har-2 + Har-6; ^{4}*J*=2.0 Hz); 7.95 (1H, s, H-5) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ = 47.4, 47.8, 26.6, 57.2, 57.9, 112.9, 119.2, 124.1, 130.7, 135.7, 153.1, 180.9 ppm. FT-IR (ATR): ν = 2951, 1547, 1444, 1259, 1220, 1122, 841, 754, 644, 558 cm^{-1}.
4b	182-183 dec.	100	^{1}H NMR (DMSO-*d*$_6$): δ = 1.35 (6H, t, 2CH$_3$); 3.86 (4H, q, 2CH$_2$); 7.83 (2H, d, Har-2 + Har-6; ^{4}*J*=2.1 Hz); 7.96 (1H, s, H-5) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ = 17.5, 53.6, 54.5, 26.6, 57.2, 57.9, 113.1, 119.2, 124.2, 130.9, 135.6, 153.2, 181.1 ppm. FT-IR (ATR): ν = 2949, 1554, 1452, 1439, 1238, 1130, 838, 750, 654 cm^{-1}.
4e	146-147 dec.	100	^{1}H NMR (DMSO-*d*$_6$): δ = 3.87 (8H, m, 4CH$_2$); 7.86 (2H, d, Har-2 + Har-6; ^{4}*J*=2.0 Hz); 7.95 (1H, s, H-5) ppm. ^{13}C NMR (DMSO-*d*$_6$): δ = 53.7, 54.1, 64.4, 112.7, 119.4, 124.0, 130.4, 135.9, 153.0, 181.0 ppm. FT-IR (ATR): ν = 2954, 1551, 1454, 1441, 1239, 1134, 842, 754, 658 cm^{-1}.

4-hydroxyacetophenone, following a two step synthetic procedure. The synthesis of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (**1**) has been accomplished by the previously reported selective monobromination of the side chain [40]. The reactions of *w*-bromoacetophenones with salts of dithiocarbamic acid, readily available from the reaction of secondary amine with carbon disulfide [60], represent an accessible way to various substituted phenacyl carbodithioates. Thus, phenacyl dithiocarbamates **2a**,**b**,**e** were obtained by reacting 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (**1**) with *N,N*-dimethylammonium *N,N*-dimethyldithiocarbamate, sodium *N,N*-diethyldithiocarbamate and morpholinium morpholine-4-carbodithioate, respectively (scheme 1). Dithiocarbamates **2c** and **2d** were synthesized according to the reported experimental procedure [61]. 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 the appearance of new signals at high fields corresponding to the hydrogen atoms in the dithiocarbamic moieties. ^{13}C NMR spectra indicate the appearance of additional signals above the 190 ppm, attributed to the thiocarbonyl group.

1,3-Dithiolium perchlorates **3** have been synthesized as colourless crystals by cyclization of dithiocarbamates **2**, in the presence of a H_2SO_4–CH_3CO_2H (1:3, v/v) mixture, followed by addition of 70% perchloric acid to the reaction medium (scheme 1). The cyclization of dithiocarbamates **2** is accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1640 cm^{-1}) and the presence of a new, strong and broad, absorption band at ca. 1100 cm^{-1}, corresponding to the perchlorate anion. ^{1}H NMR spectra of 1,3-dithiolium-2-yl perchlorates indicate the absence of the methylene hydrogen from compounds **2** (ca. 4.7-4.8 ppm) and appearance of a new signal at a low field (ca. 7.9 ppm) corresponding to the hydrogen atom from the 5-position of the heterocycle (table 2). ^{13}C NMR spectra also support the cyclization of dithiocarbamates **2** to the corresponding of 1,3-dithiolium salts by disappearance of the signals of carbonyl and thiocarbonyl atoms from dithiocarbamates spectra and appearance of a new signal at a very low field (ca. 181 ppm) which correspond to the electron deficient C-2 atom.

Treatment of these perchlorates with a saturated $NaHCO_3$ solution gives the corresponding phenolates **4** as yellow crystalline products, which show mesoionic character [47,50] (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% perchloric acid 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**

In a previous paper [47], 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 the above 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 intramolecular nature of the charge-transfer band was proved by measurements at different concentrations. Comparative analysis of UV-Vis absorption spectra of perchlorates **3** and mesoionic phenolates **4** confirm the previous findings (e.g. fig. 1).

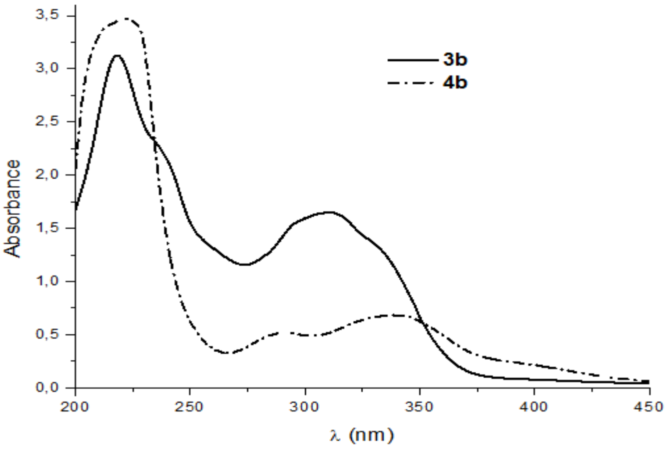


Fig. 1. UV/Vis absorption spectra of 1,3-dithiolium salt **3b** and mesoionic phenolate **4b** in ethanol

While the intramolecular charge-transfer UV-Vis absorption of such chromophores results from a charge transfer from the HOMO of the donor part to the LUMO of the acceptor part, the electronic effects of the substituents on the extended delocalization of the negative charge should result on a HOMO orbital of lower energy. The presence of a hydroxyl substituent in the *para*-position induces an extended delocalization of the negative charge up to the C(4)-C(5) bond of the dithiolium ring. In comparison with the result reported for the unsubstituted 4-hydroxyphenyl derivatives [47], the spectrum of 1,3-dithiolium perchlorate **3b** indicate a bathochromic shift induced by the bromine substituents on the p ® p* absorption band from 290 nm to 310 nm that overlaps the band corresponding to the n ® p* transitions. The charge transfer absorption band of mesoionic phenolates **4** (380 nm) is overlapped by the large absorption band centered at 338 nm. As a result of the extended conjugation, the spectrum of mesoionic phenolate **4b** indicates a new absorption band at 291 nm that belongs to the contribution of the *para*-quinoid structure to the real state of the molecule.

Conclusions

Novel 4-(3,5-dibromo-4-hydroxyphenyl)-2-(*N,N*-dialkylamino)-1,3-dithiol-2-ylium perchlorates have been synthesized by the cyclocondensation of the 1-(3,5-dibromo-4-hydroxyphenyl)-1-oxaethan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the corresponding substituted *w*-bromoacetophenone with various salts of dithiocarbamic acids. UV-Vis investigations proved the intramolecular charge transfer for the mesoionic 1,3-dithiolium phenolates and revealed a *para*-quinoid structure for mesoionic phenolates **4**.

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