Synthesis and Structural Characterization of Some 1,3-Dithiol-2-ylium Salts

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*A new series of 2-(dialkylamino)-1,3-dithiol-2-ylium cations derived from acetophenones and propiophenones was synthesized by the intramolecular condensation of appropriate substituted dithiocarbamates. The structural characterization of the new compounds has been performed by NMR and IR analysis. The structure of 1,3-dithiol-2-ylium perchlorate **3e** has been proved by X-Ray analysis.*

Keywords: acetophenones, propiophenones, carbodithioates, 1,3-dithiolium salts

Heterocyclic structures have significant implications in biological and material chemistry [1-5]. Amongst these, sulfur and nitrogen-containing heterocycles receive a great deal of attention [6-16]. In the field of conducting materials charge-transfer [17-22] and push-pull [23-38] compounds have important applications. 1,3-Dithiolium derivatives have been found to exhibit an excellent biological activity, especially against gram-positive and gram-negative bacteria [39]. Additionally, 1,3-dithiolium salts can be used as building blocks for tetrathiafulvalenes synthesis, these being good π-electron donors for organic metals [40]. The implication of TTFs as donor groups in intramolecular charge-transfer complexes has *email:been recently reviewed [41]. In this context, different types of acceptor units were investigated in terms of the nature of cationic moieties. Special interest was devoted to the systems where the donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety [42].

Accounting the above information, here are reported new 2-(*N*,*N*-dialkylamino)-1,3-dithiol-2-ylium compounds derived from acetophenones and propiophenones.

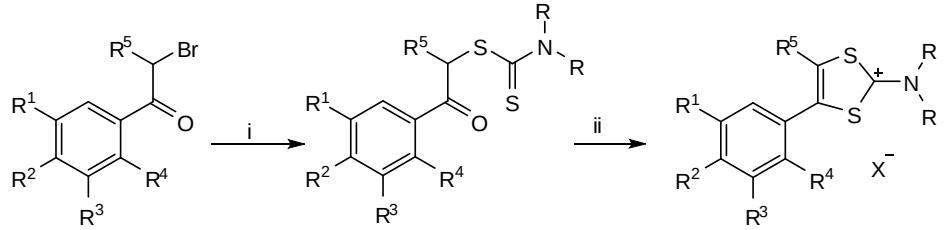
Experimental part

I. Analysis

Melting points:KSPI melting-point meter, uncorrected. IR: Bruker Tensor 27 instrument. NMR: Bruker 300 MHz spectrometer. Chemical shifts are reported in ppm downfield from TMS.

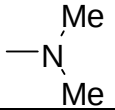
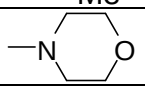
b. Synthesis

The 1,3-dithiolium cations **3a-e** have been synthesized following the reaction pathway described in Scheme 1.



1 **2** **3**

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

1, 2, 3	**R 1**	**R 2**	**R 3**	**R 4**	**R 5**	**-NR2**	**X**
a	Br	H	Br	OH	H		HSO_4
b	Br	H	Br	OH	H		HSO_4

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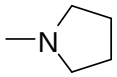
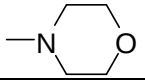
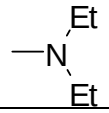
c	Br	H	H	OH	Me		HSO_4
d	Br	H	H	OH	Me		HSO_4
e	Me	OH	H	H	H		ClO_4

Scheme 1. Synthesis of 1,3-dithiolium salts **3a-e**

*c. X-ray Structure Determination of **3e**:*

Numerical details are presented in Table 1 [43].

The intensity data of **3e** was collected on a Stoe IPDS 2T diffractometer with MoK radiation. The data were collected with the Stoe XAREA program using ω-scans [44]. The space groups were determined with the XRED32 program [44]. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97 [45,46].

Table 1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **3e**

Empirical formula	C_{14} H_{18} Cl N O_5 S_2	
Formula weight	379.86	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.068(2) Å	α= 90°
	b = 13.377(3) Å	β= 91.32(3)°
	c = 12.133(2) Å	γ= 90°
Volume	1633.7(6) $Å^3$	
Z	4	
Density (calculated)	1.544 Mg/m^3	
Absorption coefficient	0.513 mm^{-1}	
F(000)	792	
Crystal size	0.38 x 0.24 x 0.18 mm^3	
Theta range for data collection	2.02 to 29.22°	
Index ranges	-12<=h<=13, -18<=k<=17, -16<=l<=16	
Reflections collected	13089	
Independent reflections	4391 [R(int) = 0.0526]	
Completeness to theta = 29.22°	98.9 %	
Absorption correction	Sphere	
Max. and min. transmission	0.7453 and 0.7431	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4391 / 0 / 215	
Goodness-of-fit on F^2	0.888	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0595	
R indices (all data)	R1 = 0.0761, wR2 = 0.0654	
Largest diff. peak and hole	0.312 and -0.405 e.$Å^{-3}$	

4-(3,5-Dibromo-2-hydroxyphenyl)-2-N,N-dimethylamino-1,3-dithiol-2-ylium hydrogen sulphate (**3a**); *General Procedure*

To a mixture of sulfuric acid (98%, 1mL) and glacial acetic acid (3mL), 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxaethan-2-yl-*N*,*N*-dimethyldithiocarbamate (**2a**, 0.83g, 2mmol) was added. The reaction mixture was heated at 75 °C for 15 min. After cooling, methyl acetate (100mL) was added in order to isolate the corresponding hydrogen sulphate. The precipitate was filtered and dried off. Recrystallization from ethanol (100mL) provided the desired compounds as colorless solids; yield 0.84g (85%). Characterization data of 1,3-dithiolium cations **3a-d** are presented in Table 2.

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM CATIONS **3a-d**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d*6), ppm
3a	208-209 dec.	85	2957, 1641, 1441, 1350, 1247, 1220, 1140, 851, 777, 688, 564	*^{1}H NMR* δ : 3.51 (6H, s, $2CH_3$); 7.58 (1H, d, H4); 7.62 (1H, d, H6, J_{H4-H6}=2.3 Hz); 8.06 (1H, s, H-5); 10.68 (1H, s, OH). *^{13}C NMR* δ : 47.1, 47.7, 112.3, 114.5, 122.7, 123.4, 130.1, 133.1, 136.4, 150.5, 186.8

3b	91-92	70	2948, 1638, 1438, 1314, 1254, 1241, 1204, 1110, 849, 768, 678, 568	*^{1}H NMR* δ : 3.94 (8H, m, $4CH_2$); 7.68 (1H, d, H4); 7.74 (1H, d, H6, J_{H4-H6}=2.3 Hz); 8.11 (1H, s, H-5); 11.22 (1H, s, OH). *^{13}C NMR* δ : 54.1, 54.5, 64.4, 112.1, 114.1, 123.8, 123.9, 130.4, 132.8, 136.9, 150.4, 187.1
3c	192-193 dec.	83	3041, 15548, 1419, 1238, 1047, 848, 601, 554	*^{1}H NMR* δ : 2.11 (4H, m, $2CH_2$), 2.31 (3H, s, CH_3-5), 3.61 (4H, m, $2CH_2$), 6.79 (1H, d, H3), 7.49 (2H, m, H4+H6), 10.11 (1H, bs, OH). *^{13}C NMR* δ : 15.1, 26.4, 56.7, 57.4, 110.4, 118.2, 118.7, 127.6, 133.0, 133.7, 135.4, 155.4, 179.5
3d	105-106 dec.	84	2941, 1638, 1439, 1318, 1241, 1214, 1131, 849, 777, 678, 551	*^{1}H NMR* δ : 2.28 (3H, s, CH_3); 3.80 (4H, m, $2CH_2$); 3.90 (4H, m, $2CH_2$); 7.11 (1H, d, H3; J_{H3-H4}=8.2 Hz); 7.55 (2H, m); 10.81 (1H, s, OH). *^{13}C NMR* δ : 15.1, 54.5, 54.7, 64.7, 65.1, 110.7, 117.8, 119.1, 127.0, 132.3, 133.1, 135.7, 155.1, 185.4

Results and discussions

Usually, 1,3-dithiol-2-ylium salts are synthesized in two steps, as described in Scheme 1: the synthesis of phenacyl dithiocarbamates, followed by acid catalyzed cyclization. The key precursors for phenacyl dithiocarbamates **2a-e** are 2-bromo-1-(3.5-dibromo-2-hydroxyphenyl)ethan-1-one [47], 2-bromo-1-(5-bromo-2-hydroxyphenyl)propan-1-one [48], and 2-bromo-1-(4-hydroxy-3-methylphenyl)ethan-1-one [49] compounds that have been synthesized according to the reported procedures. Phenacyl carbodithioates are obtained by the reactions of the salts of dialkyldithiocarbamic acid with the above mentioned ω-bromoacetophenones [50]. Following this synthetic strategy dithiocarbamates **2a-e** were obtained in good yields.

The next step for the synthesis of 1,3-dithiol-2-ylium salts **3a-e** consists in the acid catalyzed ring closure of the phenacyl carbodithioates. Several synthetic methods have been previously reported, including those for sensitive starting materials [51]. Using a mixture of concentrated sulfuric acid-glacial acetic acid (1:3 v/v) the cyclocondensation of carboditioates **2a-e** takes place under mild reaction conditions. After 15 min at 75 °C a homogeneous reaction mixture was obtained. 1,3-Dithiolium hydrogen sulphates **3a-d** have been isolated as white solids by adding water to the crude reaction products. Usual work-up provides 1,3-dithiolium sulphates **3a-d** as colorless solids, in good yields (Scheme 1, Table 2). The synthesis of 1,3-dithiolium perchlorate **3e** has been previously reported [49]. 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. 1645 cm^{-1}) and the presence of a new absorption band at ca. 1100 cm^{-1}, corresponding to the hydrogen sulphate anion in salts **3a-d**. ^{1}H NMR spectra of the new synthesized 1,3-dithiol-2-ylium salts indicate the absence of the α-carbonyl hydrogen from compounds **2**. ^{13}C NMR spectra also support the cyclization of dithiocarbamates **2** to the corresponding 1,3-dithiolium salts by the disappearance of the carbonyl and thiocarbonyl atoms from dithiocarbamates spectra and the appearance of a new signal at a very low field (180-187 ppm) which correspond to the electron deficient C(2) atom.

The structure of 4-(4-hydroxy-3-methylphenyl)-2-*N*,*N*-diethylamino-1,3-dithiol-2-ylium perchlorate (**3e**) [49] has unambiguously proved by X-ray crystallography (Figure 1). Crystal data are presented in Table 1. The recorded data confirms the nature of C(2) atom of 1,3-dithiolium ring the dihedral angle N-C(1)-S(1) and N-C(1)-S(2) being 122.64(13) and 122.11(14), respectively.

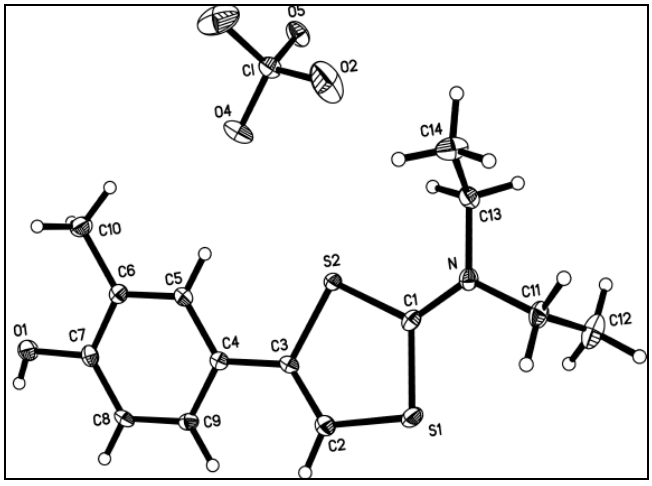


Fig. 1. Molecular structure of compound **3e**. Ellipsoids represent 50% probability levels. Selected molecular dimensions (Å, °): C(1)-N 1.308(2), S(2)-C(1) 1.7262(17), S(1)-C(1) 1.720(2), C(3)-C(4) 1.472(2)

Conclusions

The synthesis of new of 2-(dialkylamino)-1,3-dithiol-2-ylium compounds derived from acetophenones and propiophenones was performed by the heterocondensation of the corresponding phenacyl carbodithioates. The structure of the target compounds have been proved by NMR and MS analysis. The structure of one 1,3-dithiol-2-ylium perchlorate has been proved by X-Ray analysis.

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