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Solvatochromism of mesoionic iodo(1,3-dithiol-2-ylium-4-yl)phenolates

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Abstract Novel mesoionic phenolates were synthesized *via* 4-hydroxyaryl-1,3-dithiolium salts and characterized spectroscopically by UV-Vis. The bathochromic effect induced by iodine substituents was investigated for several solvents. A negative solvatochromism was recorded for the intramolecular charge transfer absorption band.

Keywords Dithiocarbamates; Dithiolium salts; Mesoionic compounds; Charge transfer.

Introduction

Solvatochromic dyes have played an important role in the understanding of solvent polarity effects and are increasingly important as probes of complex biological systems [1–3]. The systems where a donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety received special interest [4]. A variety of acceptor units have been investigated with special attention paid to cationic systems, such as pyridinium and bipyridinium cations [5–7].

In this context, investigations of a series of 2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolates have shown that 1,3-dithiolium cations can also serve as acceptor moieties in intramolecular charge transfer complexes [8]. The above mesoionic compounds showed only a small negative solvatochromism ($-\Delta\lambda = 10$–15 nm). Therefore, by varying the nature of substituents, we decided to investigate the influence of both acceptor and donor moieties on the intramolecular charge transfer absorption band. Several mesoionic phenolates with different secondary amines (dimethylamino, diethylamino, piperidine, morpholine) at the 2-position of the 1,3-dithiol-2-ylium ring were synthesized and investigated spectroscopically by UV-Vis. Since the position of intramolecular charge transfer absorption band was not affected by the nature of secondary amine moiety we decided to introduce iodine substituents on the donor part of the mesoionic 2-(1,3-dithiol-2-ylium-4-yl)phenolates. This paper deals with the synthesis and UV-Vis behavior of new iodo substituted 2-(2-dialkylamino-1,3-dithiol-2-ylium-4-yl)-phenolates.

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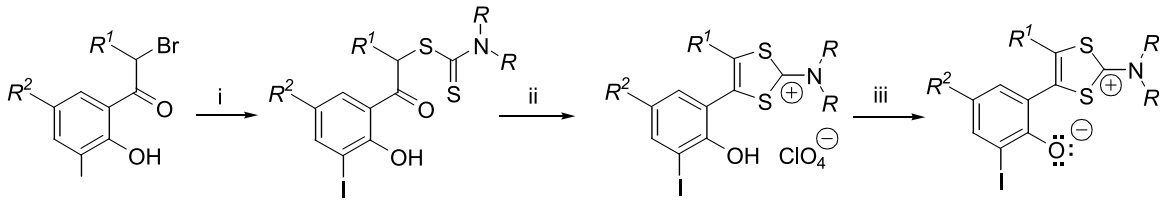
Results and discussion

Phenacyl *N*,*N*-dialkyldithiocarbamates **2a**–**2f** have been prepared by reaction of ω-bromo-ketones **1a**–**1c** with the corresponding *N*,*N*-dialkyldithiocarbamates (Scheme 1). 2-Bromo-1-(2-hydroxy-3-iodo-5-methylphenyl)butan-1-one (**1c**) has been obtained by bromination of 1-(2-hydroxy-3-iodo-5-methylphenyl)butan-1-one [9] in glacial acetic acid as the solvent.

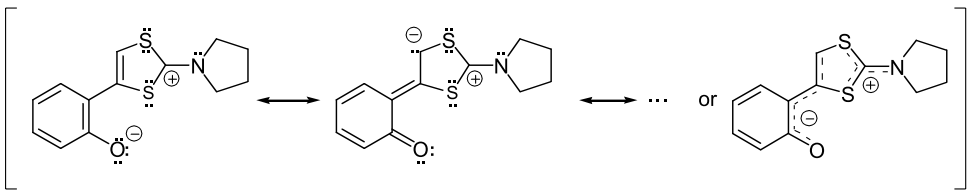
As previously reported, attempts to cyclize *N*,*N*-dialkyldithiocarbamates **2** using common cyclization agents according to literature [10–12], led to degradation of the substrates, often accompanied by loss of molecular iodine. Using a P_2O_5 – CH_3SO_3H (1:10) mixture as cyclization agent proved to be a



i. $R_2C(S)S^-$ Na^+; ii. P_2O_5 – CH_3SO_3H, 30 min., rt, CH_3COOCH_3, 70% $HClO_4$; iii. aq. $NaHCO_3$.

	R	R	R^1	R^2
a	CH_3	CH_3	H	I
b	C_2H_5	C_2H_5	CH_3	I
c		$(CH_2)_5$	CH_3	I
d	$(CH_2)_2$-O-$(CH_2)_2$		CH_3	I
e		$(CH_2)_5$	C_2H_5	CH_3
f	$(CH_2)_2$-O-$(CH_2)_2$		C_2H_5	CH_3

Scheme 1



Scheme 2

proper way to obtain 1,3-dithiolium salts **3** as pure compounds and in high yields. Furthermore, we have found that the cyclocondensation takes place in high yields even at room temperature. Thus, a suspension of **2** in three parts of the ''superacid'' mixture was stirred at room temperature for 30 min to give a solution, which contained the corresponding 1,3-dithiolium cation. Addition of 70% perchloric acid and methyl acetate to this solution give perchlorates **3a**–**3f** as white crystalline products (Scheme 2). Treatment of these perchlorates with a saturated $NaHCO_3$ solution gives the corresponding phenolates **4a**–**4f** as yellow crystalline products, which show mesoionic character [13–15] (Scheme 1).

In a previous paper [8], 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 (Scheme 2).

Investigations of UV-Vis absorption spectra of mesoionic phenolates **4a**–**4f** confirm the previous findings. In comparison to the corresponding unsubstituted phenolates, the absorption spectra of **4a**–**4f** reveal a new absorption band at 255 nm. Our initial assumptions placed the contribution of a quinoid structure to 2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolates around 235 nm, partially overlapped by the π-π^* absorption band of aromatic ring. The known bathochromic effect induced by iodine substituents confirms the above; the absorption band placed at 255 nm clearly belongs to the contribution of quinoid structures to the ground state of **4a**–**4f**.

Usually, 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. For this reason, the position of the charge-transfer band should depend on solvent polarity [16–19], defined here as the overall solvation ability of a solvent. In comparison to the above studied unsubstituted (1,3-dithiol-2-ylium-4-yl)phenolates, iodo substituted phenolates

4a–**4f** should have a HOMO orbital of lower energy and therefore a larger solvatochromism.

From the common solvents of the $E_T(30)$ solvent polarity scale [20–24], methanol was found as the highest polarity solvent, which ensures a sufficient concentration for UV-Vis measurements. In this solvent, a bathochromic effect was also recorded for the intramolecular charge transfer absorption band, 390 nm *vs* 375 nm, in unsubstituted mesoionic phenolates. In acetonitrile, a solvent of intermediate polarity, the UV-Vis spectra of phenolates **4** display a pronounced bathochromic shift of the charge-transfer band. The highest shift was recorded in *THF*, a low-polarity solvent. Thus, with increasing solvent polarity, a hypsochromic band shift of $\Delta\lambda = -44$ to -54 nm for representative phenolates **4a**, **4d**, and **4e** is observed, corresponding to a negative solvatochromism (Fig. 1, Table 1).

These results suggest a decrease in the ionization energy of the phenolate moiety because of electronic effects of substituents in both, aromatic ring and C-5 atom of the 1,3-dithiol-2-ylium ring. On going from mesoionic compound **4a** to **4d** and **4e**, the electronic density at C-5 changes significantly, with the experimentally observed hypsochromic charge-transfer band shift with increasing solvent polarity as a consequence.

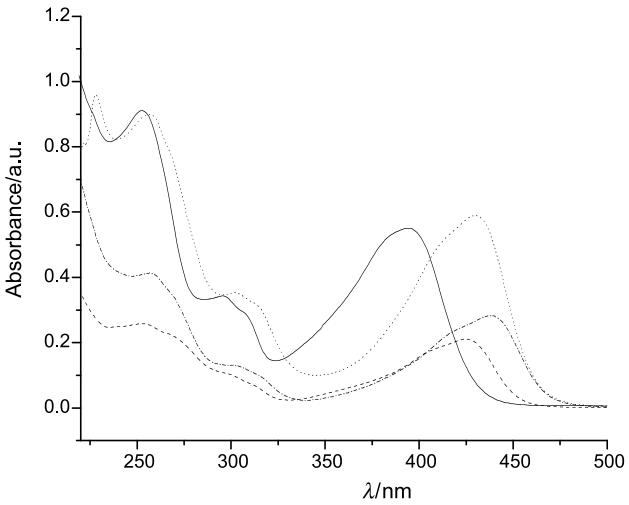


Fig. 1 UV-Vis absorption spectra of mesoionic phenolate **4a** in different solvents (—— *Me*OH; – – – – *Me*CN; ····· Me_2Cl_2; -·-·-· *THF*)

Table 1 Long-wavelength, solvent dependent charge-transfer absorption maxima, λ_{max}/nm, of mesoionic phenolates **4a**, **4d**, and **4e**, measured at 25°C and at normal pressure

	7a	**7d**	**7e**
*Me*OH	394	371	360
*Me*CN	425	409	405
Me_2Cl_2	430	413	406
THF	438	425	409
$\Delta\lambda$ nm	−44	−54	−49

The intramolecular nature of charge-transfer band of mesoionic phenolates **4** was proved by measurements at different concentrations. Although an important hypsochromic shift of the charge-transfer absorption band is induced by the iodine substituents on the donor part, better results may be achieved in systems with an extended positive charge delocalization. By replacing the secondary amine substituent with an appropriate one (*e.g.* aromatic units) the energy of LUMO orbital should increase do to the extended delocalization of positive charge. Therefore a larger solvatochromism should be recorded. The synthesis of such systems is under evaluation.

In conclusion, an improved method for cyclocondensation of some iodo-substituted phenacyl *N*,*N*-dialkyldithiocarbamates is described. These compounds exhibit a larger negative solvatochromism than previously reported unsubstituted systems.

Experimental

Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker DPX-300 spectrometer. Chemical shifts are reported in ppm downfield from *TMS*. UV-Vis absorption spectra were recorded on a Varian Cary 100 Bio spectrophotometer. Elemental analyses (C, H, N, S) were conducted using the CE440 Elemental Analyser; their results were found to be in good agreement (±0.2%) with the calculated values.

2-Bromo-1-(2-hydroxy-3-iodo-5-methylphenyl)butan-1-one (**1c**, $C_{11}H_{12}BrIO_2$)

To a solution of 10 g 1-(2-hydroxy-3-iodo-5-methylphenyl)butan-1-one (32 mmol) in 200 cm^3 glacial acetic acid a solution of 1.7 cm^3 bromine (32 mmol) in 10 cm^3 glacial acetic acid was added under vigorous stirring. After decoloration the reaction mixture was poured into 300 cm^3 water and the solid was filtered off, dried, and recrystallized from *Et*OH. Yellow crystals (8.5 g, 69%) were obtained. Mp 109–110°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.11$ (t, $J = 7.2$ Hz, CH_3), 1.95 (m, CH_2), 2.29 (s, CH_3), 5.23 (t, $J = 7.2$ Hz, CH), 7.83 (d, $J = 2.1$ Hz, H_{ar}-4), 7.90 (d, $J = 2.1$ Hz, H_{ar}-6), 12.82 (s, OH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 10.1$ (CH_3), 20.3 (CH_3), 25.9 (CH_2), 57.1 (CH), 84.6 (CH_{ar}), 126.9 (CH_{ar}), 130.1 (CH_{ar}), 131.9 (CH_{ar}), 144.5 (CH_{ar}), 163.3 (CH_{ar}), 194.5 (C) ppm; IR (ATR): $\bar{\nu} = 3438$, 2948, 1634, 1457, 1157, 862, 721, 679 cm^{-1}.

2-(2-Hydroxy-3,5-diiodophenyl)-2-oxoethyl-N,N-dimethyldithiocarbamate (**2a**, $C_{11}H_{11}I_2NO_2S_2$). *General Procedure*
To a solution of 2.34 g 2-bromo-1-(2-hydroxy-3,5-diiodophenyl)ethan-1-one (**1a**) (5 mmol) in 50 cm^3 acetone a solution of 0.72 g sodium *N,N*-dimethyldithiocarbamate (5 mmol) in 10 cm^3 water/acetone (1:1) was added. The reaction mixture was refluxed for 10 min, cooled and the obtained solid filtered, washed with water, and dried. Recrystallization from 45 cm^3 dioxane gave yellow pale crystals, 1.8 g (72%) **2a**; mp 193–194°C (dec); ^{1}H NMR (*DMSO*-d_6): $\delta = 3.33$ (s, CH_3), 3.43 (s, CH_3), 4.95 (s, CH_2), 8.24 (d, $J = 2.3$ Hz, H_{ar}-4), 8.42 (d, $J = 2.3$ Hz, H_{ar}-6), 12.46 (s, 1H, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 44.1$ (CH_2), 48.8 (CH_3), 49.2 (CH_3), 81.3 (C_{ar}), 87.7 (C_{ar}), 121.8 (C_{ar}), 138.3 (C_{ar}), 153.3 (C_{ar}), 161.1 (C_{ar}), 191.27 (C), 198.6 (C) ppm; IR (ATR): $\bar{\nu} =$ 3440, 2938, 1633, 1478, 1238, 1145, 979, 759, 696 cm^{-1}.

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxopropan-2-yl-N,N-dimethyldithiocarbamate (**2b**, $C_{14}H_{17}I_2NO_2S_2$)
Yield 88%, pale yellow crystals; mp 128–129°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.24$ (t, $J = 5.5$ Hz, $2CH_3$), 1.55 (d, $J = 6.7$ Hz, CH_3); 3.71 (q, $J = 5.5$ Hz, CH_2–N), 4.01 (q, $J = 5.5$ Hz, CH_2–N), 5.77 (q, $J = 6.7$ Hz, CH), 8.20 (d, $J = 2.3$ Hz, H_{ar}-4), 8.31 (d, $J = 2.3$ Hz, H_{ar}-6), 12.80 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 12.1$ (CH_3), 12.6 (CH_3), 17.5 (3-C), 47.5 (CH_2–N), 50.8 (CH_2–N), 51.4 (2-C), 80.5 (3-C_{ar}), 87.8 (5-C_{ar}), 120.2 (1-C_{ar}), 139.0 (6-C_{ar}), 152.2 (4-C_{ar}), 160.1 (2-C_{ar}), 193.4 (C), 199.0 (C) ppm; IR (ATR): $\bar{\nu} =$ 3445, 2934, 1631, 1481, 1236, 1139, 985, 757, 689 cm^{-1}.

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxapropan-2-yl-piperidine-1-carbodithioate (**2c**, $C_{15}H_{17}I_2NO_2S_2$)
Yield 88%, pale yellow crystals; mp 134–135°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.54$ (d, $J = 6.6$ Hz, CH_3), 1.66 (m, $3CH_2$), 4.04 (m, $2CH_2$–N), 5.78 (q, $J = 6.7$ Hz, CH), 8.19 (d, $J = 2.4$ Hz, H_{ar}-4), 8.31 (d, $J = 2.4$ Hz, H_{ar}-6), 12.79 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 17.5$ (CH_3), 23.5 (CH_2), 24.3 (CH_2), 24.5 (CH_2), 51.5 (CH_2), 52.5 (CH_2–N), 54.2 (CH_2–N), 82.0 (C_{ar}), 89.4 (C_{ar}), 125.5 (C_{ar}), 138.9 (C_{ar}), 151.6 (C_{ar}), 160.7 (C_{ar}), 193.0 (C), 198.2 (C) ppm; IR (ATR): $\bar{\nu} = 3446$, 2935, 1634, 1448, 1232, 1147, 972, 783, 695 cm^{-1}.

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxopropan-2-yl-morpholine-4-carbodithioate (**2d**, $C_{14}H_{15}I_2NO_3S_2$)
Yield 72%, pale yellow crystals; mp 173–174°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.54$ (d, $J = 6.7$ Hz, CH_3), 3.73 (m, $2CH_2$), 4.08 (m, $2CH_2$), 5.78 (q, $J = 6.7$ Hz, CH), 8.19 (d, $J = 2.3$ Hz, H_{ar}), 8.32 (d, $J = 2.3$ Hz, H_{ar}), 12.68 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 17.3$ (CH_3), 51.1 (CH_2), 51.9 (CH_2–N), 52.0 (CH_2–N), 66.5 (CH_2–O), 66.5 (CH_2–O), 81.5 (C_{ar}), 90.3 (C_{ar}), 122.2 (C_{ar}), 140.1 (C_{ar}), 152.1 (C_{ar}), 162.1 (C_{ar}), 191.8 (C), 198.4 (C) ppm. IR (ATR): $\bar{\nu} = 3446$, 2939, 1632, 1425, 1231, 1151, 982, 781, 710 cm^{-1}.

1-(2-Hydroxy-3-iodo-5-methylphenyl)-1-oxobutan-2-yl-piperidine-1-carbodithioate (**2e**, $C_{17}H_{22}INO_2S_2$)
Yield 68%, yellow pale crystals; mp 182–183°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 0.98$ (t, $J = 7.3$ Hz, CH_3), 1.68 (m, $3CH_2$), 2.01 (m, CH_2), 2.26 (s, CH_3), 4.06 (m, $2CH_2$–N), 5.82 (t, $J = 7$ Hz, CH), 7.80 (d, $J = 2.2$ Hz, H_{ar}), 7.86 (d, $J = 2.2$ Hz, H_{ar}), 12.80 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 11.9$ (CH_3), 20.4 (CH_3), 23.2 (CH_2), 24.3 (CH_2), 24.5 (CH_2), 24.6 (CH_2), 52.3 (CH_2–N), 54.1 (CH_2–N), 56.6 (2-C), 86.3 (3-C_{ar}), 118.2 (C_{ar}), 130.2 (C_{ar}), 130.8 (C_{ar}), 146.8 (C_{ar}), 159.4 (C_{ar}), 194.4 (C), 203.1 (C) ppm. IR (ATR): $\bar{\nu} = 3452$, 2940, 1634, 1434, 1229, 1152, 975, 786, 709 cm^{-1}.

1-(2-Hydroxy-3-iodo-5-methylphenyl)-1-oxobutan-2-yl-morpholine-4-carbodithioate (**2f**, $C_{16}H_{20}INO_3S_2$)
Yield 70%, yellow pale crystalls; mp 146–147°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.01$ (t, $J = 7.3$ Hz, CH_3), 2.01 (m, CH_2), 2.29 (s, CH_3), 3.76 (m, $2CH_2$), 4.13 (m, CH_2), 5.84 (t, $J = 7$ Hz, CH), 7.80 (d, $J = 2.1$ Hz, H_{ar}), 7.86 (d, $J = 2.1$ Hz, H_{ar}), 12.71 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 11.8$ (CH_3), 20.4 (CH_3), 24.6 (CH_2), 50.9 (CH_2–N), 51.8 (CH_2–N), 56.4 (CH_2), 66.2 (CH_2–O), 66.4 (CH_2–O), 86.4 (C_{ar}), 118.2 (C_{ar}), 130.5 (C_{ar}), 130.9 (C_{ar}), 146.8 (C_{ar}), 159.5 (C_{ar}), 194.2 (C), 203.0 (C) ppm; IR (ATR): $\bar{\nu} = 3448$, 2940, 1634, 1429, 1231, 1150, 968, 786, 695 cm^{-1}.

2-(Dimethylamino)-4-(2-Hydroxy-3,5-diiodophenyl)-1,3-dithiol-2-ylium perchlorate (**3a**, $C_{11}H_{10}ClI_2NO_5S_2$). *General Procedure*
To a mixture of 3 cm^3 P_2O_5–CH_3SO_3H (1:10) 1.01 g dithiocarbamate **2a** (2 mmol) were added in several portions. The reaction mixture was stirred for 30 min at room temperature. To the homogeneous mixture 0.5 cm^3 70% $HClO_4$ were added and the crude **3a** was precipitated with 50 cm^3 *Ac*O*Me*. This was filtered off, dried, and recrystallized from 100 cm^3 *Et*OH to give the pure product as white crystals, 1.08 g (92%). Mp 209–210°C (dec); ^{1}H NMR (*DMSO*-d_6): 3.51 (s, CH_3), 3.53 (s, CH_3), 7.88 (d, $J = 1.8$ Hz, H_{ar}), 8.02 (s, CH), 8.12 (d, $J = 1.8$ Hz, H_{ar}), 10.42 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 47.3$ (CH_3), 47.7 (CH_3), 85.5 (C_{ar}), 92.8 (C_{ar}), 121.6 (CH), 122.7 (C_{ar}), 132.9 (C), 137.1 (C_{ar}), 147.9 (C_{ar}), 153.5 (C_{ar}), 186.9 (C) ppm; IR (ATR): $\bar{\nu} = 3441$, 2943, 1577, 1448, 1273, 1087 (b), 846, 623 cm^{-1}.

Compounds **3b**–**3f** were obtained using the same experimental conditions.

2-(Diethylamino)-4-(2-hydroxy-3,5-diiodophenyl)-5-methyl-1,3-dithiol-2-ylium perchlorate (**3b**, $C_{14}H_{16}ClI_2NO_5S_2$)
Yield 84%, white crystals; mp 159–160°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.32$ (t, $J = 7.3$ Hz, CH_3), 1.35 (t, $J = 7.0$ Hz, CH_3), 2.23 (s, CH_3), 3.82 (q, $J = 7.3$ Hz, CH_2), 3.87 (q, $J = 7.0$ Hz, CH_2), 7.64 (d, $J = 1.9$ Hz, H_{ar}), 8.14 (d, $J = 1.9$ Hz, H_{ar}), 10.24 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 10.8$ (CH_3), 10.8 (CH_3), 15.2 (CH_3), 53.6 (CH_2), 53.7 (CH_2), 83.2 (C_{ar}), 91.33 (C_{ar}), 118.8 (C), 127.2 (C_{ar}), 134.3 (C), 139.6 (C_{ar}), 148.4 (C_{ar}), 155.6 (C_{ar}), 184.3 (C) ppm; IR (ATR): $\bar{\nu} = 3345$, 2998, 1542, 1450, 1095 (b), 851, 613 cm^{-1}.

4-(2-Hydroxy-3,5-diiodophenyl)-5-methyl-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**3c**, $C_{15}H_{16}ClI_2NO_5S_2$)
Yield 85%, white crystals; mp 190–191°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.67$ (m, CH_2), 1.82 (m, $2CH_2$), 2.24 (s, CH_3), 3.83

(m, $2CH_2$), 7.62 (d, $J = 2.0$ Hz, H_{ar}), 8.16 (d, $J = 2.0$ Hz, H_{ar}), 10.32 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): 15.3 (CH_3), 21.6 (CH_2), 24.9 (CH_2), 56.5 (CH_2–N), 57.1 (CH_2–N), 83.9 (C_{ar}), 91.2 (C_{ar}), 118.9 (C), 126.7 (C_{ar}), 134.0 (C), 139.7 (C_{ar}), 148.5 (C_{ar}), 155.4 (C_{ar}), 184.8 (C) ppm; IR (ATR): $\bar{\nu} = 3339$, 1545, 1451, 1248, 1088 (b), 885, 624 cm^{-1}.

4-(2-Hydroxy-3,5-diiodophenyl)-5-methyl-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate (**3d**, $C_{14}H_{14}ClI_2NO_6S_2$)
Yield 95%, white crystals; mp 216–217°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 2.23$ (s, CH_3), 3.42 (m, $2CH_2N$), 3.86 (m, $2CH_2O$), 7.63 (d, $J = 2.1$ Hz, H_{ar}), 8.17 (d, $J = 2.1$ Hz, H_{ar}), 10.28 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 15.3$ (CH_3), 54.2 (CH_2–N), 54.3 (CH_2–N), 65.0 (CH_2–O), 84.0 (C_{ar}), 91.3 (C_{ar}), 119.1 (C), 126.5 (C_{ar}), 134.1 (C), 139.8 (C_{ar}), 148.6 (C_{ar}), 155.3 (C_{ar}), 186.0 (C) ppm; IR (ATR): $\bar{\nu} = 3252$, 1549, 1455, 1289, 1105 (b), 884, 623 cm^{-1}.

4-Ethyl-5-(2-hydroxy-3-iodo-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**3e**, $C_{17}H_{21}ClINO_5S_2$)
Yield 83%, white crystals; mp 197–198°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.25$ (t, $J = 7.6$ Hz, CH_3), 1.80 (m, CH_2), 1.94 (m, $2CH_2$), 2.26 (s, CH_3), 2.64 (q, $J = 7.6$ Hz, CH_2), 3.85 (m, $2CH_2$), 6.28 (s, OH), 7.02 (d, $J = 2.0$ Hz, H_{ar}), 7.64 (d, $J = 2.0$ Hz, H_{ar}) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.6$ (CH_3), 19.8 (CH_3), 21.5 (CH_2), 23.3 (CH_2), 24.7 (CH_2), 56.4 (CH_2–N), 56.6 (CH_2–N), 77.2 (C_{ar}), 86.7 (C_{ar}), 114.3 (C), 126.7 (C_{ar}), 132.2 (C_{ar}), 132.2 (C), 142.0 (C_{ar}), 151.5 (C_{ar}), 185.4 (C) ppm; IR (ATR): $\bar{\nu} =$ 3381, 2951, 2874, 1525, 1444, 1272, 1091 (b), 863, 621 cm^{-1}.

4-Ethyl-5-(2-hydroxy-3-iodo-5-methylphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate (**3f**, $C_{16}H_{19}ClINO_6S_2$)
Yield 94%, white crystals; mp 187–188°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.25$ (t, $J = 7.5$ Hz, CH_3), 2.27 (s, CH_3), 2.64 (q, $J = 7.5$ Hz, CH_2), 3.44 (m, $2CH_2N$), 3.87 (m, $2CH_2O$), 7.57 (d, $J = 2.0$ Hz, H_{ar}), 8.09 (d, $J = 2.0$ Hz, H_{ar}), 10.33 (s, OH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 14.7$ (CH_3), 19.9 (CH_3), 21.5 (CH_2), 54.6 (CH_2–N), 55.0 (CH_2–N), 65.2 (CH_2–O), 84.1 (C_{ar}), 91.5 (C_{ar}), 119.2 (C), 126.6 (C_{ar}), 134.5 (C), 139.8 (C_{ar}), 148.75 (C_{ar}), 155.8 (C_{ar}), 186.5 (C) ppm; IR (ATR): $\bar{\nu} = 3375$, 2942, 1532, 1450, 1268, 1098 (b), 859, 630 cm^{-1}.

2-[2-(Dimethylamino)-1,3-dithiol-2-ylium-4-yl]-4,6-diiodophenolate (**4a**, $C_{11}H_9I_2NOS_2$). *General Procedure*
To a saturated sodium hydrogencarbonate solution 0.59 g perchlorate **3a** (1 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*/*AcOMe* afforded the pure product as yellow crystals, 0.49 g (100%). Mp 208–209°C (dec); ^{1}H NMR (*DMSO*-d_6): $\delta = 3.50$ (s, CH_3), 3.52 (s, CH_3), 7.67 (d, $J = 1.9$ Hz, H_{ar}), 8.00 (s, CH), 8.10 (d, $J = 1.9$ Hz, H_{ar}) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 47.1$ (CH_3), 47.5 (CH_3), 85.3 (C_{ar}), 92.6 (C_{ar}), 121.3 (C), 122.4 (C_{ar}), 132.8 (C), 137.4 (C_{ar}), 147.2 (C_{ar}), 153.1 (C_{ar}), 186.3 (C) ppm; IR (ATR): $\bar{\nu} = 3432$, 2926, 1551, 1439, 1267, 1062, 863 cm^{-1}.

Compounds **4b**–**4f** were obtained in the same experimental conditions.

2-[2-(Diethylamino)-5-methyl-1,3-dithiolium-4-yl]-4,6-diiodophenolate (**4b**, $C_{14}H_{15}I_2NOS_2$)
Yield 100%, yellow crystals; mp 192–193°C (dec); ^{1}H NMR (*DMSO*-d_6): $\delta = 1.31$ (t, $J = 7.2$ Hz, CH_3), 1.34 (t, $J = 7.2$ Hz, CH_3), 2.23 (s, CH_3-5), 3.82 (q, $J = 7.2$ Hz, CH_2), 3.87 (q, $J =$ 7.2 Hz, CH_2), 7.62 (d, $J = 1.9$ Hz, H_{ar}), 8.12 (d, $J = 1.9$ Hz, H_{ar}) ppm; ^{13}C NMR (*DMSO*-d_6): 10.35(CH_3), 10.4 (CH_3), 15.3 (CH_3), 53.8 (CH_2), 53.9 (CH_2), 83.3 (C_{ar}), 91.2 (C_{ar}), 118.3 (C), 127.1 (C_{ar}), 134.5 (C), 139.8 (C_{ar}), 148.6 (C_{ar}), 155.6 (C_{ar}), 184.0 (C) ppm; IR (ATR): $\bar{\nu} = 3410$, 2943, 1550, 1456, 1259, 1132 cm^{-1}.

4,6-Diiodo-2-[5-methyl-2-(piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4c**, $C_{15}H_{15}I_2NOS_2$)
Yield 100%, yellow crystals; mp 194–195°C (dec); ^{1}H NMR (*DMSO*-d_6): $\delta = 1.76$ (m, $3CH_2$), 2.23 (s, CH_3), 3.85 (m, $2CH_2$), 7.60 (d, $J = 2.0$ Hz, H_{ar}), 8.15 (d, $J = 2.0$ Hz, H_{ar}) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 15.2$ (CH_3), 21.3 (CH_2), 24.6 (CH_2), 56.3 (CH_2–N), 57.0 (CH_2–N), 83.3 (C_{ar}), 91.2 (C_{ar}), 118.7 (C), 126.3 (C_{ar}), 133.9 (C), 139.2 (C_{ar}), 148.6 (C_{ar}), 155.3 (C_{ar}), 184.3 (C) ppm; IR (ATR): $\bar{\nu} = 3407$, 2951, 2865, 1465, 1259, 1139, 1023, 881 cm^{-1}.

4,6-Diiodo-2-[5-methyl-2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**4d**, $C_{14}H_{13}I_2NO_2S_2$)
Yield 100%, yellow crystals; mp 184–185°C (dec); ^{1}H NMR (*DMSO*-d_6): $\delta = 2.22$ (s, CH_3), 3.44 (m, $2CH_2N$), 3.84 (m, $2CH_2O$), 7.61 (d, $J = 2.0$ Hz, H_{ar}), 8.15 (d, $J = 2.0$ Hz, H_{ar}) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 15.2$ (CH_3), 54.3 (CH_2–N), 65.5 (CH_2–O), 83.8 (C_{ar}), 91.3 (C_{ar}), 119.1 (C), 126.3 (C_{ar}), 134.6 (C), 139.3 (C_{ar}), 148.9 (C_{ar}), 155.3 (C_{ar}), 186.2 (C) ppm; IR (ATR): $\bar{\nu} = 3407$, 2926, 1553, 1439, 1268, 1121, 1044, 886 cm^{-1}.

2-[5-Ethyl-2-(piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]-6-iodo-4-methylphenolate (**4e**, $C_{17}H_{20}INOS_2$)
Yield 100%, yellow crystals; mp 173–174°C (dec); ^{1}H NMR ($CDCl_3$): 1.22 (t, $J = 7.5$ Hz, CH_3), 1.76 (m, CH_2), 1.87 (m, $2CH_2$), 2.24 (s, CH_3), 2.69 (q, $J = 7.5$ Hz, CH_2), 3.67 (m, CH_2), 3.73 (m, CH_2), 6.94 (d, $J = 1.6$ Hz, H_{ar}), 7.58 (d, $J =$ 1.6 Hz, H_{ar}) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.8$ (CH_3), 19.8 (CH_3), 21.7 (CH_2), 23.6 (CH_2), 24.9 (CH_2), 56.0 (CH_2–N), 77.4 (C_{ar}), 90.6 (C_{ar}), 115.9 (C), 128.5 (C_{ar}), 131.3 (C_{ar}), 137.8 (C), 141.4 (C_{ar}), 155.9 (C_{ar}), 185.4 (C) ppm; IR (ATR): $\bar{\nu} = 3415$, 2951, 2848, 1534, 1465, 1259, 1095, 863 cm^{-1}.

2-[5-Ethyl-2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]-6-iodo-4-methylphenolate (**4f**, $C_{16}H_{18}INO_2S_2$)
Yield 100%, yellow crystals; mp 87–88°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.23$ (t, $J = 7.6$ Hz, CH_3), 2.25 (s, CH_3), 2.63 (q, $J =$ 7.6 Hz, CH_2), 3.47 (m, $2CH_2N$), 3.92 (m, $2CH_2O$), 7.51 (d, $J = 1.8$ Hz, H_{ar}), 8.05 (d, $J = 1.8$ Hz, H_{ar}) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 14.2$ (CH_3), 19.7 (CH_3), 21.3 (CH_2), 54.8 (CH_2–N), 65.0 (CH_2–O), 84.0 (C_{ar}), 91.9 (C_{ar}), 119.3 (C), 126.3 (C_{ar}), 134.0 (C), 139.3 (C_{ar}), 148.0 (C_{ar}), 156.0 (C_{ar}),

185.3 (C) ppm; IR (ATR): $\bar{\nu} = 3410$, 2946, 1528, 1458, 1263, 1075, 871 cm^{-1}.

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