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Synthesis of Mesoionic 4-Methyl-2-(1,3-dithiol-2-ylium-4-yl)phenolates

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Abstract: Mesoionic 4-methyl-2-(2-amino-1,3-dithiol-2-ylium-4-yl)phenolates were synthesized *via* the corresponding 1,3-dithiolium salts. The synthesis of water soluble 1,3-dithiolium chlorides was accomplished through the corresponding mesoionic phenolates.

Keywords: Dithiocarbamates; 1,3-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 σ- or π-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]

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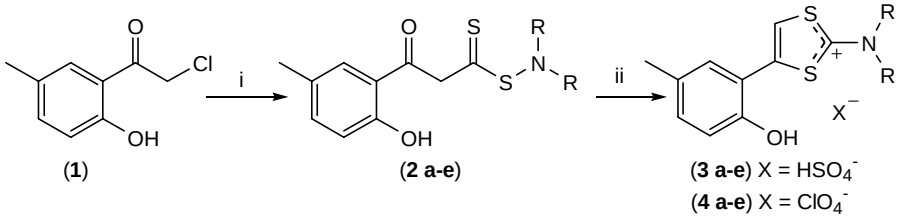
In this context, investigations of a series of 2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolates have shown that 1,3-dithiolium cations can also serve as acceptor moieties in intramolecular charge transfer complexes.[8] The above mesoionic compounds showed only a small negative solvatochromism (- $\Delta\lambda$ = 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 various substituents on the donor part of the mesoionic 2-(1,3-dithiol-2-ylium-4-yl)phenolates. A previous paper reports the synthesis and UV-Vis behavior of new iodo substituted 2-(2-dialkylamino-1,3-dithiol-2-ylium-4-yl)-phenolates.[9] This paper deals with the synthesis with methyl substituted (1,3-dithiol-2-ylium-4-yl)phenolates.

Results and Discussion

The cyclization of some 1-(2-hydroxyary1)-2-(*N*,*N*-dialkylamino-carboditioate)-1-ethanones in the presence of a H_2SO_4 – CH_3COOH mixture (1 : 3 vol.) was reported by us.[10] Despite our previous attempts we were able to isolate 1,3-dithiolium hydrogensulfates (**3a-e**) as stable solid compounds. The synthesis of 1,3-dithiolium salts (**3**) and (**4**) is described in Scheme 1.

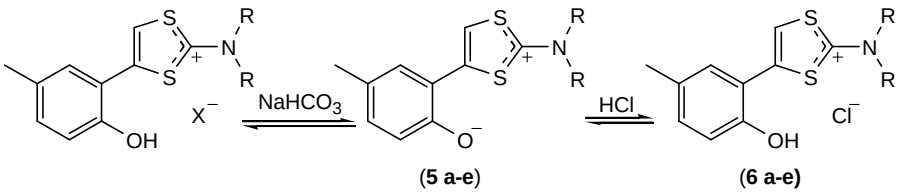


(**1**) (**2 a-e**) (**3 a-e**) X = HSO_4^-
(**4 a-e**) X = ClO_4^-

Scheme 1

(**2**), (**3**), (**4**), (**5**), (**6**)	**R**	**R**
a	CH_3	CH_3
b	CH_2CH_3	CH_2CH_3
c	$(CH_2)_4$	
d	$(CH_2)_5$	
e	$(CH_2)_2$-O-$(CH_2)_2$	

Treatment of perchlorates (**4a-e)** under heterogeneous conditions, with saturated aqueous potassium hydrogencarbonate solution affords 4-methyl-2-(1,3-dithiol-2-ylium-4-yl)phenolates (**5a-e**), in quantitative yields. The molecular structure of the new compounds was proved by analytical and spectral data and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compounds (**5a-e**) with 70% perchloric acid regenerates the 1,3-dithiolium perchlorates in quantitative yields (Scheme 2). 4-Methyl-2-(1,3-dithiol-2-ylium-4-yl)phenolates were isolated as yellow crystalline products that present the features of mesoionic compounds.[11-13] The presence of a hydroxy substituent in an *ortho*-position induces an extended delocalization of the negative charge up to the C(4)-C(5) bond of the dithiolium ring.



(**5 a-e**) (**6 a-e**)

Scheme 2

Furthermore, we have been able to isolate the 1,3-dithiolium chlorides (**6a-e**) using the interconversion possibilities between the mesoionic phenolates and its salts. Thus, 4-(2-hydroxy-5-methylphenyl)-1,3-dithiolium chlorides have been isolated as a solid crystalline product by the treatment of an acetonic suspension of (**5**) with 37% hydrochloric acid (Scheme 2).

Conclusions

We have reported the synthesis of mesoionic 4-methyl-2-(2-amino-1,3-dithiol-2-ylium-4-yl)phenolates *via* the corresponding 1,3-dihiolium salts. Intramolecular charge transfer properties of these compounds are under investigation. This paper also presents the synthesis of 1,3-dithiolium chlorides as solid compounds.

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. 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. Mass spectra were recorded on a Finnigan MAT 90X spectrometer.

1-(2-Hydroxy-5-methylphenyl)-1-oxaethan-2-yl-pyrrolidine-1-carbodithioate (**2c**)*; General Procedure*

To a solution of 2-chloro-1-(2-hydroxy-5-methylphenyl)ethan-1-one (**1**, 3.68 g, 0.02 mol) in acetone (30 mL) a solution of pyrrolidinium pyrrolidine-1-carbodithioate (4.36 g, 0.02 mol) in acetone-water (1:1, 60 mL) was added. After 5 min under stirring at room temperature the precipitate was filtered, washed with water and dried off. Recrystallization from ethanol (200 mL) gave colorless crystals; yield 4.9 g (83%).

Mp 140-141 °C. IR (ATR): 2848, 1644, 1588, 1437, 1339, 1257, 1156, 988, 830, 667 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 1.81 (s, 3H, CH_3-5), 3.24 (t, ^{3}J = 7.5 Hz, 2H, CH_2), 3.40 (t, ^{3}J = 7.5 Hz, 2H, CH_2), 4.43 (s, 2H, CH_2), 6.37 (d, ^{3}J = 9.4 Hz, 1H, H-3), 6.80 (dd, ^{3}J = 9.4 Hz, ^{4}J = 2.5 Hz, 1H, H-4), 7.24 (d, ^{4}J = 2.5 Hz, 1H, H-6), 11.15 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6, 22.1, 54.7, 62.2, 120.9, 125.4, 130.2, 131.7, 135.2, 154.5, 196.5, 204.3. MS (ESI): *m/z* = 295 (M^+).

2-(2-Hydroxy-5-methylphenyl)-2-oxoethyl-N,N-dimethyldithio-carbamate (**2a**):

Yield 87%. Mp 151-152 °C. IR (ATR): 2850, 1638, 1485, 1368, 1245, 1170, 972, 826, 773, 668 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3-5), 3.37 (s, 3H, CH_3-N), 3.40 (s, 3H, CH_3-N), 4.82 (s, 2H, CH_2), 6.81 (d, ^{3}J = 9.3 Hz, 1H, H-3), 7.25 (dd, ^{3}J = 9.3 Hz, ^{4}J = 2.3 Hz, 1H, H-4), 7.67 (d, ^{4}J = 2.3 Hz, 1H, H-6), 11.53 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 43.5, 62.8, 118.7, 124.5, 130.5, 131.5, 135.5, 154.0, 194.5, 203.5. MS (ESI): *m/z* = 269 (M^+).

2-(2-Hydroxy-5-methylphenyl)-2-oxoethyl-N,N-diethyldithio-carbamate (**2b**):

Yield 72%. Mp 93-94 °C. IR (ATR): 2940, 1646, 1484, 1341, 1260, 1203, 1168, 975, 738, 668 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, 3H, CH_3), 1.23 (t, 3H, CH_3), 2.23 (s, 3H, CH_3-5), 3.81 (q, 2H, CH_2), 3.95 (q, 2H, CH_2), 4.83 (s, 2H, CH_2), 6.80 (d, ^{3}J = 9.0 Hz, 1H, H-3), 7.29 (dd, ^{3}J = 9.0 Hz, ^{4}J = 2.3 Hz, 1H, H-4), 7.69 (d, ^{4}J = 2.3 Hz, 1H, H-6), 11.57 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4, 18.6, 47.5, 62.3, 118.5, 124.7, 130.0, 131.2, 136.0, 153.7, 193.8, 204.1. MS (ESI): *m/z* = 297 (M^+).

1-(2-Hydroxy-5-methylphenyl)-1-oxaethan-2-yl-piperidine-1-carbodithioate (**2d**):

Yield 82%. Mp 135-136 °C. IR (ATR): 2914, 1632, 1614, 1469, 1432, 1399, 1229, 1169, 973, 818, 700, 668 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (m, 6H, $3CH_2$), 2.29 (s, 3H, CH_3-5), 4.13 (m, 4H, $2CH_2$), 4.92 (s, 2H, CH_2), 6.88 (d, ^{3}J = 9.1 Hz, 1H, H-3), 7.32 (dd, ^{3}J = 9.1 Hz, ^{4}J = 2.4 Hz, 1H, H-4), 7.75 (d, ^{4}J = 2.4 Hz, 1H, H-6), 11.62 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 24.1, 25.1, 54.5, 62.1, 118.9, 124.9, 130.1, 132.1, 135.0, 153.9, 195.2, 204.8. MS (ESI): *m/z* = 309 (M^+).

1-(2-Hydroxy-5-methylphenyl)-1-oxaethan-2-yl-morpholine-1-carbodithioate (**2e**):

Yield 75%. Mp 140-141 °C. IR (ATR): 2847, 1634, 1487, 1485, 1295, 1263, 1114, 993, 741 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3-5), 3.75 (m, 4H, CH_2-O-CH_2), 4.12 (m, 4H, CH_2-N-CH_2), 4.97 (s, 2H, CH_2), 6.83 (d, ^{3}J = 10.1 Hz, 1H, H-3), 7.32 (dd, ^{3}J = 10.1 Hz, ^{4}J = 2.3 Hz, 1H, H-4), 7.77 (d, ^{4}J = 2.3 Hz, 1H, H-6), 11.34 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1, 58.2, 62.1, 68.5, 115.9, 124.4, 130.5, 132.0, 135.5, 153.2, 194.3, 204.1. MS (ESI): *m/z* = 311 (M^+).

4-(2-Hydroxy-5-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium hydrogensulfate (**3c**); *General Procedure*

To a mixture of conc sulfuric acid (1 mL) and glacial acetic acid (3 mL) 1-(2-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-pyrrolidine-1-carbodithioate (**2c**, 1 g, 3.38 mmol) was added in small portions. The reaction mixture was heated at 80 °C for 10 min, cooled and diluted with methyl acetate (50 mL). The precipitate was filtered, washed with water and dried off. Recrystallization from ethanol (150 mL) gave colorless crystals; yield 1.2 g (95%).

Mp 234-235 °C. IR (ATR): 2919, 1560, 1515, 1222, 1141, 1051, 843, 573 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.25 (m, 7H, CH_3-5 + $2CH_2$), 3.77 (m, 4H, $2CH_2$), 5.75 (s, 2H, HSO_4 + OH), 6.90 (d, ^{3}J = 8.9 Hz, 1H, H-3), 7.1 (dd, ^{3}J = 8.9 Hz, ^{4}J = 2.2 Hz, 1H, H-4), 7.30 (d, ^{4}J = 2.2 Hz, 1H, H-6), 8.02 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 25.9, 26.1, 56.3, 56.7, 116.3, 116.6, 118.7, 128.3, 128.8, 132.1, 135.5, 151.5, 181.6. MS (ESI): *m/z* = 278 (M^{+}-HSO_4).

2-(Dimethylamino)-4-(2-Hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium hydrogensulfate (**3a**):

Yield 85%. Mp 225-226 °C. IR (ATR): 3100, 1578, 1156, 1061, 1019, 852, 566 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.26 (s, 3H, CH_3-5), 3.54 (s, 3H, CH_3), 3.57 (s, 3H, CH_3), 5.79 (s, 2H, HSO_4 + OH), 6.94 (d, ^{3}J = 8.0 Hz, 1H, H-3), 7.21 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.4 Hz, 1H, H-4), 7.44 (d, ^{4}J = 2.4 Hz, 1H, H-6), 8.01 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.9, 46.7, 47.1, 116.3, 116.6, 116.8, 128.3, 128.8, 132.1, 135.5, 154.5, 184.6. MS (ESI): *m/z* = 252 (M^{+}-HSO_4).

2-(Diethylamino)-4-(2-Hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium hydrogensulfate (**3b**):

Yield 89%. Mp 201-202 °C. IR (ATR): 2952, 1544, 1499, 1230, 1140, 1058, 850, 829, 577 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.36 (t, 6H,

$2CH_3$), 2.27 (s, 3H, CH_3-5), 3.84 (q, 2H, CH_2), 3.91 (q, 2H, CH_2), 5.50 (s, 2H, HSO_4 + OH), 6.90 (d, ^3J = 8.2 Hz, 1H, H-3), 7.15 (dd, ^3J = 8.2 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.41 (d, ^4J = 2.3 Hz, 1H, H-6), 8.01 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.5, 22.3, 23.1, 46.1, 47.5, 116.3, 116.6, 116.8, 128.3, 128.8, 132.1, 135.5, 154.0, 184.1. MS (ESI): *m/z* = 280 (M^+-HSO_4).

4-(2-Hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium hydrogensulfate (**3d**):

Yield 86%. Mp 222-223 °C. IR (ATR): 2952, 1549, 1502, 1231, 1144, 1057, 850, 829, 577 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 1.80 (m, 6H, $3CH_2$), 2.26 (s, 3H, CH_3-5), 3.85 (m, 4H, $2CH_2$), 5.50 (s, 2H, HSO_4 + OH), 6.90 (d, ^3J = 7.8 Hz, 1H, H-3), 7.14 (dd, ^3J = 7.8 Hz, ^4J = 2.4 Hz, 1H, H-4), 7.30 (d, ^4J = 2.4 Hz, 1H, H-6), 8.00 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 21.2, 24.4, 55.8, 56.5 116.3, 116.5, 117.9, 128.4, 128.8, 132.1, 134.5, 151.6, 186.4. MS (ESI): *m/z* = 292 (M^+-HSO_4).

4-(2-Hydroxy-5-methylphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium hydrogensulfate (**3e**):

Yield 86%. Mp 236-237 °C (dec). IR (ATR): 3088, 1553, 1511, 1141, 1108, 1051, 849, 576 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.28 (s, 3H, CH_3-5), 3.90 (m, 8H, $4CH_2$), 5.69 (s, 2H, HSO_4 + OH), 6.93 (d, ^3J = 8.4 Hz, 1H, H-3), 7.14 (dd, ^3J = 8.4 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.29 (d, ^4J = 2.3 Hz, 1H, H-6), 8.01 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 57.5, 58.5, 68.4, 116.3, 116.5, 118.0, 128.4, 128.8, 132.1, 134.5, 151.6, 186.9. MS (ESI): *m/z* = 294 (M^+-HSO_4).

4-(2-Hydroxy-5-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4c**); *General Procedure*

To a mixture of conc sulfuric acid (3 mL) and glacial acetic acid (9 mL) 1-(2-hydroxy-5-methylphenyl)-1-oxaethan-2-yl-pyrrolidine-1-carbodithioate (**2c**, 3 g, 0.01 mol) was added in small portions. After 10 min at 80 °C perchloric acid (70%, 1.5 mL) was added and the reaction mixture was diluted with methyl acetate (100 mL). The precipitate was filtered, washed with water and dried off. Recrystallization from ethanol (225 mL) gave colorless crystals; yield 3.41 g (89%).

Mp 254-255 °C. IR (ATR): 3303, 1562, 1511, 1366, 1255, 1100, 1044, 619 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.26 (m, 7H, CH_3-5 + $2CH_2$), 3.75 (m, 4H, $2CH_2$), 6.88 (d, ^{3}J = 9.3 Hz, 1H, H-3), 7.10 (dd, ^{3}J = 9.3 Hz, ^{4}J = 2.2 Hz, 1H, H-4), 7.32 (d, ^{4}J = 2.2 Hz, 1H, H-6), 8.03 (s, 1H, H-5), 10.80 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.8, 25.9, 26.0, 56.3, 56.7, 116.3, 116.6, 118.7, 128.2, 128.8, 132.0, 135.5, 151.5, 181.5. MS (ESI): *m/z* = 278 (M^{+}-ClO_4).

2-(Dimethylamino)-4-(2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium perchlorate (**4a**):

Yield 87%. Mp 212-213 °C. IR (ATR): 3323, 1572, 1513, 1401, 1255, 1099, 1048, 620 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3H, CH_3-5), 3.55 (s, 3H, CH_3), 3.58 (s, 3H, CH_3), 6.95 (d, ^{3}J = 8.1 Hz, 1H, H-3), 7.20 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H, H-4), 7.44 (d, ^{4}J = 2.4 Hz, 1H, H-6), 8.02 (s, 1H, H-5), 10.79 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.7, 46.7, 47.1, 116.3, 116.6, 116.8, 128.3, 129.1, 132.1, 135.5, 154.5, 184.5. MS (ESI): *m/z* = 252 (M^{+}-ClO_4).

2-(Diethylamino)-4-(2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium perchlorate (**4b**):

Yield 82%. Mp 166-167 °C. IR (ATR): 3320, 1558, 1515, 1422, 1256, 1102, 1045, 618 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.37 (t, 6H,

$2CH_3$), 2.28 (s, 3H, CH_3-5), 3.85 (q, 2H, CH_2), 3.96 (q, 2H, CH_2), 6.93 (d, ^3J = 8.2 Hz, 1H, H-3), 7.17 (dd, ^3J = 8.2 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.41 (d, ^4J = 2.3 Hz, 1H, H-6), 8.01 (s, 1H, H-5), 10.82 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.8, 22.5, 23.0, 46.0, 47.1, 116.3, 116.6, 116.8, 128.3, 128.8, 132.8, 135.1, 154.9, 184.9. MS (ESI): *m/z* = 280 (M^+-ClO_4).

4-(2-Hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4d**):

Yield 81%. Mp 242-243 °C (dec). IR (ATR): 3350, 1558, 1511, 1443, 1255, 1102, 1044, 619 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 1.77 (m, 6H, $3CH_2$), 2.26 (s, 3H, CH_3-5), 3.86 (m, 4H, $2CH_2$), 6.95 (d, ^3J = 7.9 Hz, 1H, H-3), 7.19 (dd, ^3J = 7.9 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.39 (d, ^4J = 2.3 Hz, 1H, H-6), 7.97 (s, 1H, H-5), 10.70 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 21.1, 24.4, 55.9, 56.4 116.3, 116.5, 117.9, 128.4, 128.8, 132.1, 134.5, 151.6, 186.3. MS (ESI): *m/z* = 292 (M^+- ClO_4).

4-(2-Hydroxy-5-methylphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium perchlorate (**4e**):

Yield 83%. Mp 219-220 °C (dec). IR (ATR): 3354, 1552, 1509, 1438, 1257, 1099, 1046, 620 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.27 (s, 3H, CH_3-5), 3.91 (m, 8H, $4CH_2$), 6.94 (d, ^3J = 8.7 Hz, 1H, H-3), 7.18 (dd, ^3J = 8.7 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.39 (d, ^4J = 2.3 Hz, 1H, H-6), 8.03 (s, 1H, H-5), 10.68 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 57.8, 58.4, 68.4, 116.3, 116.5, 118.0, 128.4, 128.8, 132.1, 134.5, 151.6, 186.4. MS (ESI): *m/z* = 294 (M^+- ClO_4).

5-Methyl-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5c**)*; General Procedure*

To a saturated sodium hydrogencarbonate solution (15 mL) hydrogensulfate **3c** (0.59 g, 1.86 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 gave yellow crystals; yield 0.5 g (100%).

Mp 209 °C (dec). IR (ATR): 2702, 1558, 1507, 1452, 1250, 795, 626 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.27 (m, 7H, CH_3-5 + $2CH_2$), 3.77 (m, 4H, $2CH_2$), 6.88 (d, ^{3}J = 8.7 Hz, 1H, H-3), 7.08 (dd, ^{3}J = 8.7 Hz, ^{4}J = 2.3 Hz, 1H, H-4), 7.30 (d, ^{4}J = 2.3 Hz, 1H, H-6), 7.95 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 20.0, 25.9, 26.1, 56.3, 56.7, 116.3, 116.6, 118.7, 128.3, 128.8, 132.1, 135.6, 154.2, 182.1. MS (ESI): *m/z* = 277.

2-[2-(Dimethylamino)-1,3-dithiol-2-ylium-4-yl]-5-methylphenolate (**5a**):

Yield 100%. Mp 195-196 °C (dec). IR (ATR): 1582, 1412, 1297, 1257, 825, 770 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3H, CH_3-5), 3.56 (s, 3H, CH_3), 3.59 (s, 3H, CH_3), 6.94 (d, ^{3}J = 8.0 Hz, 1H, H-3), 7.21 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.4 Hz, 1H, H-4), 7.44 (d, ^{4}J = 2.4 Hz, 1H, H-6), 7.92 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.8, 46.8, 47.1, 116.3, 116.8, 116.9, 128.3, 128.8, 132.1, 135.5, 154.1, 184.9. MS (ESI): *m/z* = 251.

2-[2-(Diethylamino)-1,3-dithiol-2-ylium-4-yl]-5-methylphenolate (**5b**):

Yield 100%. Mp 203-204 °C (dec). IR (ATR): cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.35 (t, 6H, $2CH_3$), 2.27 (s, 3H, CH_3-5), 3.84 (q, 2H, CH_2), 3.90 (q, 2H, CH_2), 6.91 (d, ^{3}J = 8.0 Hz, 1H, H-3), 7.15 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.3 Hz, 1H, H-4), 7.401 (d, ^{4}J = 2.3 Hz, 1H, H-6), 7.91 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.8, 22.4, 23.2, 46.8, 47.9, 116.0, 116.5, 116.8, 128.3, 128.8, 132.1, 135.5, 153.4, 184.4. MS (ESI): *m/z* = 279.

5-Methyl-2-[2-(piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5d**):

Yield 100%. Mp 178-179 °C (dec). IR (ATR): 2850, 1553, 1501, 1439, 1252, 800 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 1.70 (m, 6H, $3CH_2$), 2.26 (s, 3H, CH_3-5), 3.87 (m, 4H, $2CH_2$), 6.92 (d, ^{3}J = 7.7 Hz, 1H, H-3), 7.15 (dd, ^{3}J = 7.7 Hz, ^{4}J = 2.4 Hz, 1H, H-4), 7.35 (d, ^{4}J = 2.4 Hz, 1H, H-6), 7.90 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 21.2, 24.4, 55.8, 56.5 116.3, 116.5, 118.2, 128.4, 128.8, 132.0, 134.5, 151.2, 186.1. MS (ESI): *m/z* = 291.

5-Methyl-2-[2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5e**):

Yield 100%. Mp 180-181 °C (dec). IR (ATR): 2518, 1575, 1523, 1258, 1115, 882, 763, 547 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.28 (s, 3H, CH_3-5), 3.90 (m, 8H, $4CH_2$), 6.90 (d, ^{3}J = 8.5 Hz, 1H, H-3), 7.18 (dd, ^{3}J = 8.5 Hz, ^{4}J = 2.3 Hz, 1H, H-4), 7.30 (d, ^{4}J = 2.3 Hz, 1H, H-6), 7.95 (s, 1H, H-5). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 57.5, 58.5, 68.4, 116.1, 116.5, 118.5, 128.4, 128.8, 132.1, 134.5, 151.2, 186.1. MS (ESI): *m/z* = 293.

4-(2-Hydroxy-5-methylphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium chloride (**6c**); *General Procedure*

To a suspension of mesoionic phenolate **5c** (0.5 g, 1.8 mmol) in acetone (10 mL) a solution of HCl (37%, 0.28 mL, 9 mmol) was added. The reaction mixture was vigorously stirred at room temperature for 2 h, then filtered and washed with acetone. Recrystallization from ethanol gave colorless crystals; yield 0.55 g (98%).

Mp 238-239 °C (dec). IR (ATR): 2707, 1560, 1508, 1450, 1256, 799, 620 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.27 (m, 7H, CH_3-5 + $2CH_2$),

3.77 (m, 4H, $2CH_2$), 6.95 (d, ^3J = 8.3 Hz, 1H, H-3), 7.14 (dd, ^3J = 8.3 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.35 (d, ^4J = 2.3 Hz, 1H, H-6), 8.07 (s, 1H, H-5), 10.55 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 26.0, 26.1, 56.3, 56.7, 116.3, 116.7, 118.7, 128.4, 128.8, 132.1, 135.5, 151.5, 181.5. MS (ESI): *m/z* = 278 (M^+-Cl).

2-(Dimethylamino)-4-(2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium chloride (**6a**):

Yield 99%. Mp 272-273 °C. IR (ATR): 1577, 1412, 1297, 1257, 826, 777 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.26 (s, 3H, CH_3-5), 3.58 (s, 3H, CH_3), 3.61 (s, 3H, CH_3), 6.99 (d, ^3J = 8.0 Hz, 1H, H-3), 7.24 (dd, ^3J = 8.0 Hz, ^4J = 2.4 Hz, 1H, H-4), 7.47 (d, ^4J = 2.4 Hz, 1H, H-6), 8.07 (s, 1H, H-5), 10.59 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.9, 46.5, 47.0, 116.3, 116.8, 116117.2, 128.3, 128.8, 132.1, 135.7, 154.0, 184.4. MS (ESI): *m/z* = 252 (M^+-Cl).

2-(Diethylamino)-4-(2-hydroxy-5-methylphenyl)-1,3-dithiol-2-ylium chloride (**6b**):

Yield 96%. Mp 168-169 °C. IR (ATR): 2095, 1573, 1410, 1292, 1251, 823, 762 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.38 (t, 6H, $2CH_3$), 2.27 (s, 3H, CH_3-5), 3.88 (q, 2H, CH_2), 3.99 (q, 2H, CH_2), 6.97 (d, ^3J = 8.1 Hz, 1H, H-3), 7.19 (dd, ^3J = 8.1 Hz, ^4J = 2.4 Hz, 1H, H-4), 7.44 (d, ^4J = 2.4 Hz, 1H, H-6), 8.05 (s, 1H, H-5), 10.52 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 18.8, 22.3, 22.9, 46.0, 47.5, 116.3, 116.6, 116.8, 128.3, 128.8, 132.0, 135.5, 154.4, 184.5. MS (ESI): *m/z* = 280 (M^+-Cl).

4-(2-Hydroxy-5-methylphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium chloride (**6d**):

Yield 98%. Mp 257-258 °C (dec). IR (ATR): 2855, 1559, 1504, 1441, 1255, 809 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 1.74 (m, 6H, $3CH_2$), 2.27 (s,

3H, CH_3-5), 3.88 (m, 4H, $2CH_2$), 6.97 (d, ^3J = 8.0 Hz, 1H, H-3), 7.20 (dd, ^3J = 8.0 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.41 (d, ^4J = 2.3 Hz, 1H, H-6), 8.01 (s, 1H, H-5), 10.59 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 21.2, 24.4, 55.8, 56.4 116.4, 116.5, 118.2, 128.4, 128.9, 132.1, 134.5, 151.6, 186.4. MS (ESI): *m/z* = 292 (M^+- Cl).

4-(2-Hydroxy-5-methylphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium chloride (**6e**):

Yield 99%. Mp 253-254 °C (dec). IR (ATR): 3318, 1570, 1529, 1253, 1106, 885, 767, 545 cm^{-1}. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.26 (s, 3H, CH_3-5), 3.93 (m, 8H, $4CH_2$), 6.96 (d, ^3J = 8.2 Hz, 1H, H-3), 7.19 (dd, ^3J = 8.2 Hz, ^4J = 2.3 Hz, 1H, H-4), 7.41 (d, ^4J = 2.3 Hz, 1H, H-6), 8.09 (s, 1H, H-5), 10.52 (s, 1H, OH). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 19.9, 57.4, 58.4, 68.4, 116.3, 116.5, 118.3, 128.4, 128.8, 132.1, 134.5, 151.4, 186.9. MS (ESI): *m/z* = 294 (M^+- Cl).

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